

Problems

# **Statistical Mechanics and Thermodynamics**

SoSe 2018

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JGU Mainz - Institut für Physik

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## 1 Undergraduate level

### Problem 1 Thermodyn.

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1. Two containers of equal volume are filled with an equal number of moles of two different ideal classical gasses. The containers are in thermal contact. The molecules of one of the gasses are diatomic, the other monoatomic. Which container has greater
  - (a) pressure
  - (b) internal energy
  - (c) heat capacity at constant volume
  - (d) entropy
2. Discuss and criticize, using examples, the following statement: "In equilibrium, nature seeks the equipartition of energy, in which each degree of freedom contains an average amount of energy  $\frac{1}{2}k_B T$ ."

### Problem 2 Stat. Mech. (classical, Fermi-Dirac, Bose-Einstein Stat.)

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1. Two containers of equal volume are filled with an equal number of moles of two different ideal monoatomic classical gasses. The containers are in thermal contact. The molecules of one of the gasses obey classical (Maxwellian, Boltzmann) statistics, while the molecules of the other gas obey Fermi-Dirac statistics. Which container has greater
  - (a) pressure
  - (b) internal energy
  - (c) heat capacity at constant volume
  - (d) entropy
2. Answer the same questions as for previous part, but comparing classical statistics and Bose-Einstein statistics. Do any of your answers depend on the temperature?

### Problem 3 Thermodyn.

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An engine with one mole of a monoatomic gas as the working fluid undergoes the following cycle:

- (a) An adiabatic expansion from pressure  $P_0$ , volume  $V_0$  to a volume  $2V_0$ ;
  - (b) An isothermal compression from  $2V_0$  to  $V_0$ ;
  - (c) At constant pressure to the original state.
1. Find the efficiency of the engine
  2. What is the change in the entropy of the gas during the second leg of the cycle?
  3. What is the change in internal energy of the gas in the first leg of the cycle?

**Problem 4 Maxwell relations**

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1. Define the thermodynamic energy function  $H$  (enthalpy),  $G$  (Gibbs free energy), and  $F$  (Helmholtz free energy) for a homogeneous system in term of  $U$  (internal energy) and the thermodynamic variables  $(S, T, P, V)$ . What are the natural variables for each function?
2. Derive the Maxwell relations between the partial derivatives of the thermodynamic variables. Justify each step in words.

**Problem 5 Thermodyn. (Cyclic process)**

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An engine with one mole of a monoatomic ideal gas as a working substance undergoes the following process:

- 1  $\rightarrow$  2 isobaric expansion  $V_0 \rightarrow 2V_0$
- 2  $\rightarrow$  3 isothermal expansion  $P_0 \rightarrow P_0/2$
- 3  $\rightarrow$  4 isobaric compression at  $P_0/2$
- 4  $\rightarrow$  1 isothermal compression at  $T_0$

1. Find the net work done in the process in terms of  $P_0, V_0$
2. Find the net heat absorbed in the total process in terms of  $P_0, V_0$
3. Find the entropy change in going from 1 to 2 in terms of  $R$
4. Find the entropy change in going from 2 to 3 in terms of  $R$
5. What is the net entropy change in the total process?

**Problem 6 Heat capacity normal metal vs. superconductor**

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The heat capacity of a normal metal  $C_n$  at low temperatures is given by  $C_n = \gamma T$ , where  $\gamma$  is a constant. If the metal is superconducting below  $T_c$ , then the heat capacity  $C_S$  in the temperature range  $0 < T < T_c$  is given by the relation  $C_S = \alpha T^3$ , where  $\alpha$  is a constant. The entropy  $S_n, S_S$  of the normal metal and superconducting metal are equal at  $T_c$ , also  $S_n = S_S$  as  $T \rightarrow 0$ .

1. Find the relation between  $C_S$  and  $C_n$  at  $T_c$ .
2. Is the transition first or second order?

**Problem 7 Thermodyn.**

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A cylinder closed at both ends equipped with insulating (adiabatic) walls, and is divided into two parts with a frictionless, insulating, movable piston. The gases on both sides are initially at equilibrium with identical pressure, volume, and temperature  $(P_0, V_0, T_0)$ . The gas is ideal with  $C_V = 3R/2$  and  $C_P/C_V = 5/3$ . By means of a heating coil in the gas on the left hand side, heat is slowly supplied to the gas on the left until the pressure reaches  $32P_0$ . In terms of  $P_0, V_0$  and  $T_0$

1. What is the final right hand volume?
2. What is the final right hand temperature?
3. What is the final left hand temperature?
4. How much heat must be supplied to the gas on the left?
5. How much work is done on the gas on the right?

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- What is entropy change of the gas on the right?
  - Compute the entropy change of the gas on the left.

### Problem 8 Carnot cycle

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This problem refers to a classical monoatomic gas.

- On a  $T - S$  diagram, draw an isothermal expansion, an isobaric expansion, and a constant volume process.
- Draw a Carnot cycle on a  $T - S$  diagram. Assume that the Carnot cycle operates between  $T_1$  and  $T_2$ , with  $T_1 > T_2$ .
- Derive the expression for the efficiency of a Carnot cycle using this  $T - S$  diagram.

### Problem 9 Van der Waals gas

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The van der Waals equation of state for a mole of gas is given by  $(P + a/V^2)(V - b) = RT$ , where  $V$  is the molar volume of the gas.

- Define the critical point  $T_c$ ,  $V_c$  and  $P_c$  in terms of  $(\partial p/\partial v)_T$  and  $(\partial^2 P/\partial V^2)_T$ .
- Express  $a$  and  $b$  in terms of  $T_c$  and  $V_c$ .
- Express  $P_c$  in terms of  $T_c$  and  $V_c$ .
- Calculate the compressibility  $\kappa_T = -V^{-1}(\partial V/\partial P)_T$  and the thermal expansion coefficient  $\beta = V^{-1}(\partial V/\partial T)_P$  for the van der Waals gas. What do these quantities do at the critical point?

### Problem 10 Clausius-Clapeyron

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- If  $l_S$  is latent heat of sublimation per mole, and the vapor phase can be considered to be an ideal gas, show by using Clausius-Clapeyron equation that

$$\frac{dP}{P} = \frac{l_S}{RT^2} dT, \quad \text{and} \quad l_S = -R \frac{d(\log P)}{d(1/T)}$$

where the volume occupied by the solid can be neglected compared to that occupied by the vapor.

- Iodine vapor can be assumed to be an ideal diatomic gas with constant  $C_P$ . At  $301K$ , the vapor pressure is  $51.5N/m^2$  and at  $299K$  it is  $43.5N/m^2$ . Compute the latent heat of sublimation at  $300K$ .
- Assuming constant latent heat, calculate the vapor pressure at  $305K$ , assuming no phase transition exist in the intervening temperature range.

### Problem 11 Heat engine

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- A body of finite, temperature independent, heat capacity is originally at temperature  $T_1$  which is higher than the temperature of a heat reservoir  $T_2$ . Suppose that a heat engine operates in infinitesimal cycles between the body and the reservoir, until it lowers the temperature of the body from  $T_1$  to  $T_2$  extracting  $Q$  (heat) and does work  $W$  during the process. Prove that the maximum amount of work obtainable is

$$W_{\max} = Q - T_2 (S_1 - S_2),$$

where  $S_1 - S_2$  is the entropy decrease of the body.

2. Two identical bodies, each of constant heat capacity  $C$  are at the same initial temperature  $T_i$ . A refrigerator operates between these two bodies until one of them is cooled to  $T_2$ . Calculate using the same principle as the one in the previous question the final temperature of the high temperature body in terms of  $T_i$  and  $T_2$ . Show that the minimum amount of work needed is

$$W = C \left( \frac{T_i^2}{T_2} + T_2 - 2T_i \right).$$

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**Problem 12 Maxwell's Relations**

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1. Write down differential equations for the internal energy  $U$ , the enthalpy  $H$ , the Helmholtz free energy  $F$ , and the Gibbs function  $G$ .
2. Derive, showing your reasoning the four Maxwell's Relations.
3. Show that

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P.$$

4. For a van der Waals gas, show that the internal energy increases as the volume increases. The van der Waals equation of state is

$$P = \frac{RT}{V-b} - \frac{a}{V^2}.$$

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**Problem 13 Thermodyn.**

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1. A membrane separates two chambers of equal volume. Only one side contains gas, the other is a vacuum. The system as a whole is thermally isolated from the world, and its walls are rigid. If the membrane is burst (neglect the energy associated with the membrane) which of the following quantities will remain unchanged after the system adjusts to the doubled volume?
  - (a) total entropy  $S$
  - (b) total particle number  $N$
  - (c) total energy  $E$
  - (d) temperature  $T$
  - (e) pressure  $P$
  - (f) chemical potential  $\mu$
2. During which periods of time can one describe the entropy of the system as a unique function of energy, volume, and particle number? Comment on your answers for each part.
  - (a) Initially.
  - (b) During the expansion.
  - (c) After the adjustment to the doubled volume.

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**Problem 14 Thermodyn. (Cyclic process)**

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What is the thermal efficiency of an engine that operates by taking an ideal gas the following cycle?

1. Start with  $n$  moles at  $P_0, V_0, T_0$ .
2. Change to  $2P_0, V_0$ , at constant volume.

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3. Change  $2P_0, 2V_0$ , at constant pressure.
  4. Change to  $P_0, 2V_0$ , at constant volume.
  5. Change  $P_0, V_0$ , at constant pressure.

### Problem 15 Entropy of water with heat source

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Heat is added to 0.5kg of ice at  $0^\circ\text{C}$  until it is all melted. If you don't know the heat of melting, call it  $l$ .

1. What is the change in entropy of the water?
2. If the source of heat is a very massive body at a temperature of  $20^\circ\text{C}$ , what is the change in entropy of this body?
3. What is the total change in entropy of the water and the heat source?

### Problem 16

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A system possesses three energy levels  $E_1 = \epsilon, E_2 = 2\epsilon, E_3 = 3\epsilon$  with degeneracies  $g(E_1) = g(E_2) = 1$  and  $g(E_3) = 2$ . Write down

1. The partition function for the system
2. The energy of the system
3. The heat capacity of the system
4. What is the "low temperature" temperature dependence of the heat capacity?
5. What is the "high temperature" temperature dependence of the heat capacity?

### Problem 17 Spin waves

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For a ferromagnetic solid at low temperatures, the quantized waves of magnetization (spin waves) have their frequency  $\omega$  related to their wave number  $k$  according to  $\omega = Ak^2$  where  $A$  is a constant.

1. For a 3-dimensional solid, write down the density of states  $D(\omega)$  for such an excitation.
2. Write an expression for the energy density for the spin waves.
3. Determine an expression for the heat capacity, and what is its temperature dependence at low temperatures?
4. At sufficiently low temperatures, which terms should give the largest contribution to the specific heat: phonons, electrons, or spin waves? Which would give the smallest contribution?

### Problem 18 Rotation of diatomic gas

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According to quantum mechanics, the molecules of a diatomic gas possess rotational energy levels

$$e_r = \hbar^2 r(r+1)/2I, \quad \text{where } r = 0, 1, 2, \dots$$

and  $I$  is a constant, the level  $r$  being  $(2r+1)$ -fold degenerate.

1. Write down the expression for the partition function of the rotational motion.

- Using the previous part find the molar rotational heat capacity of the gas at low and at high temperatures.
- For  $CO$ , the constant,  $I$  has a value  $1.3 \times 10^{-39} \text{ gm} \cdot \text{cm}^2$ . What is the molar rotational heat capacity for  $CO$  at room temperature?

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**Problem 19 Thermodyn.**

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Consider an ideal gas.

- Show that the heat transferred during an infinitesimal quasi-static process can be written as

$$dQ = \frac{C_V}{R} V dP + \frac{C_P}{R} P dV$$

- Apply the above equation to show that  $PV^\gamma = \text{const.}$  for an adiabatic process. What is  $\gamma$ ?

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**Problem 20 Cyclic processes**

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A vessel contains  $10^{-3}$  cubic meters of helium gas at  $3K$  and  $103Pa$ . Take the zero of internal energy of helium to be at this point. You may assume that helium acts as a monoatomic ideal gas.  $R = 8.31 \text{ J/mole-K}$ .

- The temperature is raised to  $300K$  at constant volume. How much heat  $Q$  is absorbed, and what is the internal energy of helium?
- The helium is now expanded adiabatically to  $3K$ . What is the final volume? How much work  $W$  is done by the gas and what is the new internal energy of the gas?
- The helium is now compressed isothermally to its original volume. What are  $Q$ ,  $W$ , and  $\Delta U$  during this process?
- Sketch the process on a  $PV$  diagram. What is the efficiency of the cycle? Compare this efficiency to that of an ideal Carnot cycle operating between the two temperature extremes.

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**Problem 21**

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On a mountainside, air is enclosed in a limp, massless, plastic bag and then is carried down  $100m$ , in a time too short for heat to flow across the plastic bag, but slow enough that the pressure inside the bag is in equilibrium with its surroundings at all times. If air weighs  $29.3 \text{ g / mole}$ , and has  $C_P = 29.3 \text{ J/K}$ , by how much does the temperature in the air change? Give a brief explanation for the sign of the rise or fall in temperature.

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**Problem 22 Surface tension of non-interacting spin**

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- Find the Fermi energy at  $T = 0$ ,  $\epsilon_F$ , of a gas of  $N$  noninteracting spin one-half particles constrained to move in two dimensions within an area  $A$ .
- Recall that the surface tension,  $\sigma$ , in two dimensions is analogous to pressure in three dimensions so that the surface tension contribution from a particle in state  $n$  is given by  $-\partial\epsilon_n/\partial A$ . Show that the surface tension at  $T = 0$  is given by  $N\epsilon_F/2A$ .

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**Problem 23 Thermodyn.**

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Derive the general expression for  $C_P - C_V$  in terms of  $\alpha_T$ ,  $K_T$  where  $\alpha_T$  is the isothermal expansion coefficient and  $K_T$  is the isothermal compressibility coefficient of the material. Prove that  $(C_P - C_V)/T$  must approach zero as  $T$  approaches zero.

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**Problem 24 Phase transition**

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The work done by a long solenoid in magnetizing a thin rod shaped magnetic sample inside it is

$$\delta W_{\text{sol}} = \mu_0 V H_a dM$$

here  $\mu_0$  is the permeability of free space,  $V$  the sample volume,  $H_a$ , the applied field and  $M$  the magnetization of the sample (magnetic moment per unit volume), The magnetic induction inside the sample is given by

$$B = \mu_0 (H_a + M) = \mu_0 (1 + \chi) H_a$$

where  $\chi$  is the magnetic susceptibility of the material. For most ordinary metals in the normal state,  $\chi$  is rather small. (For this problem it can be set equal to zero.) If the metal goes into the superconducting state, however, it would usually exhibit a Meissner effect which means that  $B = 0$  inside the superconductor, i.e.  $\chi = -1$ . At temperatures below the superconducting transition temperature,  $T < T_c$ , an applied field  $H_a = H_c$ , (the critical field) is sufficient to destroy superconductivity. The phase boundary between the superconducting state and the normal state can be approximated by

$$H_c = H_0 \left[ 1 - (T/T_c)^2 \right]$$

1. For this phase boundary in the  $H_a$ ,  $T$  plane. Write the defining expression for the magnetic Gibbs free energy  $G(T, P, H_a)$  and its differential.
2. What is the relationship between  $G_N(T, P_0, H_c)$  and  $G_s(T, P_0, H_c)$ , the Gibbs free energies for the normal and superconducting phases along this phase boundary.  $P_0$  is an arbitrary, fixed pressure at which the relation for  $H_c$ , given above was determined. Find the relationship between  $G_N(T, P_0, H_a)$  and  $G_N(T, P_0, 0)$  and between  $G_s(T, P_0, H_a)$  and  $G_s(T, P_0, 0)$ .
3. Use the results of the previous parts to show that
  - (a) there must be a jump discontinuity in the heat capacity of a metal when it undergoes the superconducting transition at  $T = T_c$ . (Relate this jump to  $dH_c/dT$  at  $T = T_c$ ,  $H_a = 0$ );
  - (b) there must be a latent heat of transformation when the superconductor is driven from the superconducting state to the normal state by a magnetic field applied at a constant temperature  $T$ . (Relate this latent heat to the slope of the phase boundary as a function of temperature.)

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**Problem 25 First law of thermodynamics**

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Starting from ideal gas law and the first law of thermodynamics, derive the relation between pressure  $P$  and volume  $V$  for an adiabatic process in terms of  $\gamma \equiv (cV + R)/C_V = c_P/C_V$ .

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**Problem 26**

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1. Assuming that water is incompressible, estimate the change in Gibbs energy  $\Delta G$  in joules of  $100 \text{ cm}^3$  of water at  $25^\circ$  when the pressure is changed from 1 atm. to 100 atm. (Note that  $1 \text{ atm.} = 1.013 \times 10^5 \text{ N/m}^2$ .)



2. In fact the volume of a sample does change when it is subjected to pressure, and so we ought to see how to take the effect into account, and then judge whether it is significant. The volume varies in a way that can be determined by specifying the isothermal compressibility  $\kappa = -V^{-1}(\partial V/\partial P)_T$ , and we may assume that this is virtually constant over a pressure range of interest. Deduce an expression for the Gibbs energy  $G_f$  at the pressure  $p_f$  in terms of its value  $G_i$  at the initial pressure  $p_i$ , the original volume of the sample  $V_i$ , and the compressibility  $\kappa$ . Take the limit of  $\kappa \rightarrow 0$  in your expression for  $\Delta G \equiv G_f - G_i$ , and show that it reduces to the expression used in the first part.

## Problem 27

A hydrogen atom in equilibrium with a radiation field at temperature  $T$  can be in its ground state orbital level (the "1 - s" level, which is two-fold spin degenerate with energy  $\epsilon_0$ ), or it can be in its first excited state energy level (the "2 - p" level, which is six-fold degenerate with energy  $\epsilon_1$ ). For the purpose of this problem we shall assume that this atom does not have any other excited states (i.e., no 2s level and no levels with the principal quantum number  $n > 2$ ).

1. (a) What is the probability that the atom will be in an "orbital s-state"?
- (b) What is the probability that the atom will be in an "orbital p-state"?
- (c) What is the probability that the atom will be in an "orbital s-level"?
- (d) What is the probability that the atom will be in an "orbital p-level"?
2. If the temperature is such that  $k_B T = \epsilon_1 - \epsilon_0$ , then show and state which of the two orbital levels is occupied more.
3. Derive an expression for the mean energy of the atom at temperature  $T$  and obtain the limiting value of this mean energy as  $T \rightarrow \infty$ .
4. Derive an expression for the entropy of the atom at temperature  $T$  and also, from the definition of entropy, state what should be the values of the entropy for this atom in the limits of  $T \rightarrow 0$  and  $T \rightarrow \infty$ . (If you do not know the answer for the last question, you may obtain the limits from your general expression of entropy.)

## Problem 28 Clausius-Clapeyron

Consider a single component system with two phases 1 and 2

1. Starting from the condition of equilibrium for the two phases that the Gibbs free energies  $g_1$  and  $g_2$  are the same, i.e.  $g_1 = g_2$ , derive the Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{l_{1,2}}{T\Delta v}$$

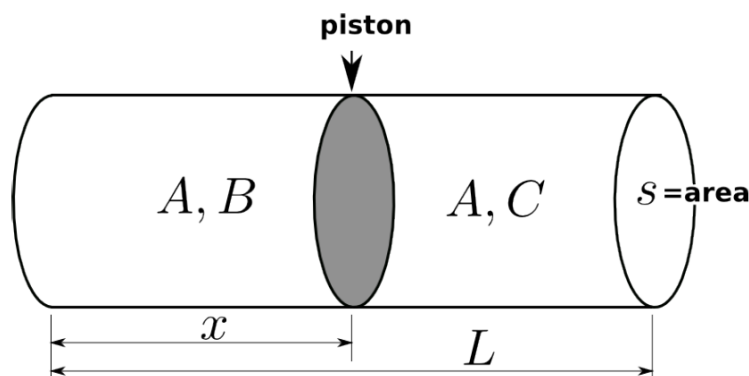
where  $l_{1,2}$  is the heat absorbed when one mole of phase 1 is transformed to phase 2,  $\Delta v = v_2 - v_1$  is the corresponding volume change, and  $P$  and  $T$  are, respectively, the pressure and temperature of the system.

2. Using the above equation show that the slope of any vapor pressure curve (liquid or solid) is positive.
3. Show that the melting curve for water has a negative slope.
4. The slope of a vapor pressure curve near the critical point is finite. Using the above equation find the expected numerical value for  $l_{1,2}$  at the critical point.

### Problem 29 Three gas system

Consider a thermally isolated cylinder of length  $l$  and area  $S$  shown in the figure. The piston is semi-permeable, allowing gas  $A$  only to pass through. The cylinder contains classical ideal gases  $A$ ,  $B$  and  $C$ , so that gas  $B$  is contained on the left, and gas  $C$  on the right, as shown. The cylinder and piston have small heat capacity compared to the gases.

1. Find the equilibrium piston position,  $x_0$ , given the mole amounts of the three gases,  $N_A, N_B, N_C$ .
2. If the piston is moved adiabatically from its equilibrium position ( $x_0$ ), find the temperature vs.  $x$ , in terms of the initial temperature  $T_0$ , and the constant volume molar heat capacities of the three gases  $C_A, C_B$ , and  $C_C$ . (Assume that the three gases attain a mutual temperature.)
3. What is the total entropy change in the process ( $S$  vs.  $x$ )?
4. For the system of  $B$  molecules only, what is the entropy change ( $S_B$  vs.  $x$ )?



### Problem 30 Non-interacting fermions

Consider a system of  $N$  non-interacting fermions for which the single-particle density of states  $\mathcal{N}(\epsilon)$  is a sum of delta functions:

$$\mathcal{N}(\epsilon) = N_0 \sum_{n=0}^{\infty} \delta(\epsilon - n\epsilon_0)$$

where  $\epsilon_0$  is a constant of the dimension of energy, and  $N_0$  is proportional to the total volume  $V$  of the system and is otherwise a dimensionless constant.

1. What is the relation which determines the chemical potential  $\mu$  of this system as a function of  $N$ ,  $V$ , and the temperature  $T$ ?
2. Sketch the dependence of  $\mu$  on  $N$  at fixed  $V$  and  $T$  assuming that  $T \ll \epsilon_0$ , so one is in the low temperature regime (but not exactly at  $T = 0$ ). You may sketch the inverse function  $N(\mu)$  if you so choose to do so.
3. What is the relation which determines the total energy  $E$  of the system as a function of  $T$ ,  $V$ , and  $\mu$ ?
4. Use the above relations to show that the total heat capacity at constant volume of the system is given by:

$$C_V = \frac{N_0 \epsilon_0^2}{4k_B T} \left\{ \sum_{n=0}^{\infty} \frac{n^2}{\cosh^2 \left[ \frac{1}{2} \beta (n\epsilon_0 - \mu) \right]} - \frac{\left[ \sum_{n=0}^{\infty} \frac{n}{\cosh^2 \left[ \frac{1}{2} \beta (n\epsilon_0 - \mu) \right]} \right]^2}{\sum_{n=0}^{\infty} \frac{1}{\cosh^2 \left[ \frac{1}{2} \beta (n\epsilon_0 - \mu) \right]}} \right\}$$

[Note:  $\cosh x \equiv \frac{1}{2} [e^x + e^{-x}]$ .]

### Problem 31

Imagine a set of  $N$  independent spins, with fixed positions and  $J = 1$ . In a uniform magnetic field, the spin energies are  $E = \mu HS$ , where  $s = (1, 0, -1)$  labels the spin component along the magnetic field,  $H$  is the applied field, and  $\mu$  is the magnetic moment.  $N$  is a very large number.

1. Find a general form for  $n^+$ ,  $n^0$ , and  $n^-$ , the expectation values for the numbers of spins with each of the three spin components, at a given temperature and field. Do not assume the high-temperature limit here.
2. What is  $\langle E \rangle$ , the total energy expectation value, in the high temperature limit (first temperature-dependent term)?
3. Find an expression for the entropy  $S$ , in the high-temperature limit. Here we are looking for two terms, the temperature-independent  $T \approx \infty$  term and the first temperature-dependent term. (You may need Stirling's approximation,  $\log N! \approx N \log N - N$ , although one can do the problem without needing this formula.)
4. From the previous result, find the temperature dependence on the field  $H$ , as  $H$  is varied in an adiabatic process. For decreasing  $H$ , what is the process called?

### Problem 32 Laws of Thermodyn.

A particular system obeys the following relations: For internal energy;

$$U = PV$$

and for the pressure,

$$P = BT^2$$

where  $V$  is volume,  $T$  absolute temperature, and  $B$  is a constant.

1. Find the fundamental equation of this system, that is how the entropy  $S$  depends on  $U$  and  $T$  and an arbitrary constant  $S_c$ .
2. Discuss and show whether  $S$  obeys the Third Law of Thermodynamics.
3. Calculate how much heat is transferred into the system when the volume changes from  $V_0$  to  $2V_0$  during an isobaric process ( $P = P_0$ ).
4. Calculate the amount of work done by the system when  $V$  changes from  $V_0$  to  $2V_0$  under isobaric condition ( $P = P_0$ ).
5. Show that your results from the previous two parts obey the First Law of Thermodynamics.

### Problem 33 Relativistic gas

Consider an extremely relativistic gas consisting of weakly interacting  $N$  identical monoatomic molecules with energy momentum relationship  $E = cp$ , where  $c$  is the speed of light. The gas is confined to a volume  $V$  and is in thermal equilibrium at temperature  $T$ .

1. Calculate the partition function  $Z_N(V, T)$  for the gas.
2. Calculate the Helmholtz free energy  $F$ .
3. Derive an equation of state of the gas.

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**Problem 34 Thermodyn.**

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Consider the properties of a rubber band with tension  $\lambda(x, T)$ , extension  $x$ , entropy  $S$ , and temperature  $T$ .

1. Find the work done by the rubber band when stretched from  $x$  to  $x + dx$ .
2. Formulate the first law of thermodynamics for the system.
3. Show that

$$\left(\frac{\partial S}{\partial x}\right)_T = -\left(\frac{\partial \lambda}{\partial T}\right)_x.$$

4. Show that

$$\left(\frac{\partial x}{\partial S}\right)_T = \left(\frac{\partial x}{\partial \lambda}\right)_T \left(\frac{\partial T}{\partial x}\right)_\lambda.$$

5. If now the rubber band obeys Hooke's law as an ideal spring, with the force constant  $K$  independent of temperature, what is implied about the functional form of  $S = S(x, T)$ ?

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**Problem 35**

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A horizontal insulating cylinder contains a frictionless, thermally insulating piston. On each side of the piston there are  $V_0$  cubic meters of a monoatomic ideal gas at a pressure  $P_0$  and absolute temperature  $T_0$ . The gas on the left hand side is heated slowly until the piston has compressed the right hand side to a pressure of  $32P_0$ .

1. How much work is done on the gas on the right hand side? Express the answer in units of  $P_0 V_0$ .
2. What is the final temperature of the gas on the right hand side in units of  $T_0$ ?
3. What is the change in entropy for the gas on the right hand side in units of the number of moles times the gas constant,  $nR$ ?
4. What is the final temperature of the gas on the left hand side in units of  $T_0$ ?
5. How much heat is added to the gas on the left hand side? Express the answer in units of  $P_0 V_0$ .

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**Problem 36 Liquid at low temperatures**

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The relation between the frequency  $\nu$  and the wavelength  $\lambda$  for surface tension waves on the surface of a liquid of density  $\rho$  and surface tension  $\sigma$  is

$$\nu^2 = \frac{2\pi\sigma}{\rho\lambda^3}$$

Use a method analogous to the Debye theory of specific heats to find a formula, analogous to the Debye  $T^3$  law, for the temperature dependence of the surface energy  $E$  of a liquid at low temperatures. The surface tension of liquid helium at  $0K$  is  $0.352 \times 10^{-3} N/m$  and its density is  $0.145 g \cdot cm^{-3}$ . From these data estimate the temperature range over which your formula for  $E(T)$  is valid for liquid helium, assuming that each helium atom in the surface of the liquid possesses one degree of freedom. You may assume

$$\int_0^\infty \frac{x^{4/3}}{e^x - 1} dx = 1.68.$$

Boltzmann's constant  $k_B = 1.38 \times 10^{-16} \text{ erg} \cdot K^{-1}$

Avogadro's number  $N = 6.02 \times 10^{23} \text{ mole}^{-1}$

Planck's constant  $\hbar = 1.05 \times 10^{-27} \text{ erg} \cdot \text{sec}$

### Problem 37 Ideal gas

One liter of an ideal gas under a pressure of 1 atm is expanded isothermally until its volume is doubled. It is then compressed to its original volume at constant pressure and further compressed isothermally to its original pressure. Plot the process on a  $P - V$  diagram and calculate the total work done on the gas. If 50J of heat, were removed during the constant- pressure process, what would be the total change in internal energy? ( $1 \text{ atm} = 1.013 \times 10^5 \text{ N/m}^2$ )

### Problem 38 Van der Waals gas

1. For a general (non-ideal) gas, derive the formula

$$dE = nC_V dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV.$$

$C_V$  is the constant-volume specific heat, assumed here to be a constant, and  $n$  denotes the number of moles of gas. You may want to use the Maxwell relation,

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V.$$

2. For the van-der-Waals equation of state,

$$\left( P + \frac{n^2 a}{V^2} \right) (V - b) = nRT,$$

derive a specific form for  $dE$  given above.  $C_V$  is again a constant (valid, presumably, over a limited temperature range).

3. Find, for the van-der-Waals gas, the constant-pressure specific heat  $C_P(T, V)$ , using your result from the previous part. Note that  $C_P$  is not a constant, but show that it reduces to the expected form for the ideal gas case.

### Problem 39

In an isolated system of  $N$  identical particles ( $N$  large) each particle can be in two energy states:  $\epsilon_1 = 0$  and  $\epsilon_2 = \epsilon > 0$ . The total energy of the system is  $E$ . Find, as a function of  $E$ ,

1. The entropy of the system.
2. The temperature of the system.

Note that  $\log n! = n \log n - n$

### Problem 40 Two phase system

A substance is found to have two phases  $N$  and  $S$ . In the normal state, the  $N$  phase, the magnetization  $M$  is negligible. At a fixed temperature  $T < T_c$ , as the external magnetic field  $H$  is lowered below the critical field

$$H_c(T) = H_0 \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]$$

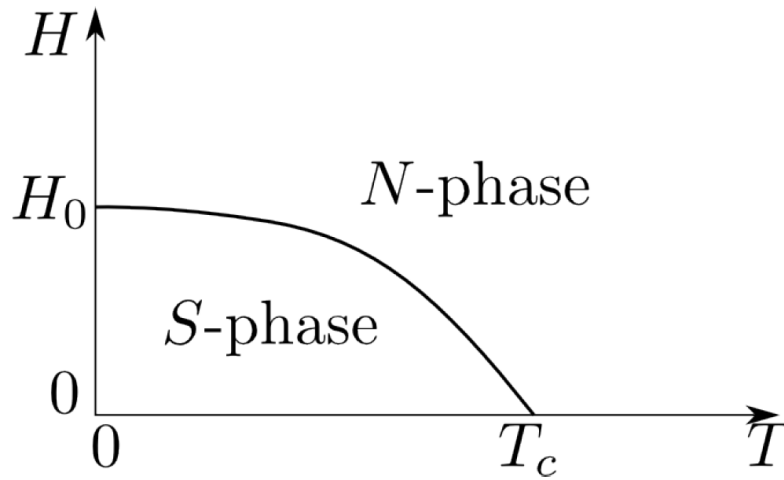
the normal state undergoes a phase transition to a new state, the  $S$  phase. In the  $S$  state, it is found that  $B = 0$  inside the material. The phase diagram is shown below.

1. Show that the difference in Gibbs free energies (in cgs units) between the two phases at temperature  $T \leq T_c$ , is given by

$$G_S(T, H) - G_N(T, H) = \frac{1}{8\pi} [H^2 - H_c^2(T)] .$$

(You may express your answer in another system of units. The Gibbs free energy in a magnetic field is given by  $G = U - TS - HM$ .)

2. Compute the latent heat of transition  $L$  from the  $N$  to the  $S$  phase.  
[Hint: one approach is to consider a "Clausius-Clapeyron" type of analysis. ]
3. At  $H = 0$ , compute the discontinuity in the specific heat as the material transforms from the  $N$  to the  $S$  phase.
4. Is the phase transition first or second order at  $H = 0$ ? What is the basis of your conclusion?



### Problem 41

A thermally conducting, uniform and homogeneous bar of length  $L$ , cross section  $A$ , density  $\rho$  and specific heat at constant pressure  $c_P$  is brought to a steady state by contact at one end with a hot reservoir at a temperature  $T_H$  and at the other end with a cold reservoir at a temperature  $T_C$ . The bar is removed from the reservoirs, thermally insulated and kept at constant pressure.

1. Find the equilibrium temperature  $T_f$  of the bar.
2. Show that the change in entropy of the bar is

$$\Delta S = C_P \left( 1 + \log T_f + \frac{T_C}{T_H - T_C} \log T_C - \frac{T_H}{T_H - T_C} \log T_H \right) ,$$

where  $C_P = c_P \rho A L$ . Assume  $c_P$  and thermal conductivity are constants.

### Problem 42 Harmonic oscillator

1. Show that the Hamiltonian of an  $LC$  circuit is that of a harmonic oscillator. Identify the resonance frequency, and obtain the discrete energy levels of this system if it is quantized.
2. Calculate the mean energy of this system if it is at thermodynamic equilibrium with its surroundings which are at an absolute temperature  $T$ .

3. Show how the root-mean-square voltage  $V_{rms}$ , across the capacitor of this circuit can be used as a thermometer to measure the absolute temperature  $T$  of its surroundings, by showing that  $V_{rms}$  is a monotonically increasing function of  $T$  and therefore  $V_{rms}$  can uniquely determine  $T$ . Neglect any temperature dependence of  $L$  or  $C$ .

### Problem 43

Find the change of temperature of a quantity of water carried by a downward current to a depth of 1km in a lake at  $27^\circ\text{C}$ . For water at this temperature

$$\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = 0.00013 \text{deg}^{-1}$$

and you may assume: "no heat exchange" ( $\Delta S = 0$ ).

Given:  $g = 980 \text{ cm/s}^2$ , and  $\rho = 1 \text{ gm/cm}^3$ ,  $c_P \sim 1 \text{ cal/g} \cdot \text{deg}$  for water, and  $1 \text{ cal} = 4.18 \times 10^7 \text{ erg}$ .

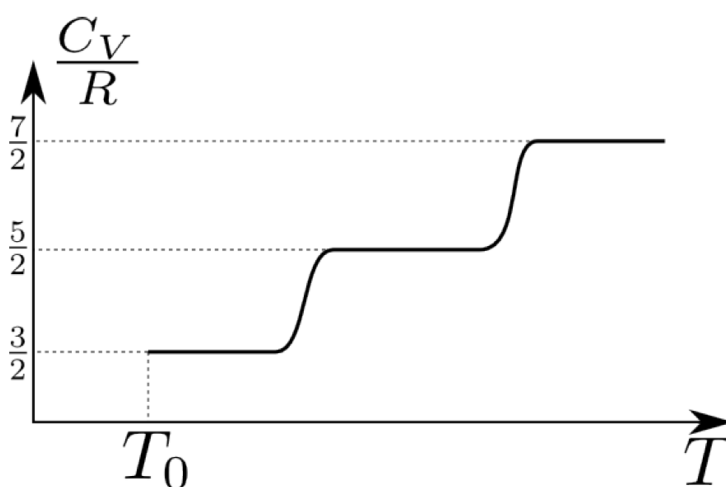
### Problem 44

Measuring the tension  $J$  of a rubber band stretched at a constant length  $l$ , it is found that  $J = AT$ , where  $A$  is a positive constant depending only on  $l$ ;  $T$  is the absolute temperature.

1. Show that the internal energy  $U$  is a function of the temperature only.
2. Show that the entropy  $S$  decreases with increasing length at constant temperature.
3. When the rubber band is stretched adiabatically, does the temperature increase, decrease or stay unchanged, and why?

### Problem 45

The molecules of one mole of a certain gas consist of two different atoms, each of zero nuclear spin, bound together. Measurements of the specific heat of this material, over a wide range of temperatures, give the graph shown below. (The values marked on the vertical scale correspond to the height of the curve in each of the plateau regions.)



1. Describe the physical reason for each of the three different plateaus in the figure.

2. At temperature  $T_0$ , the gas undergoes a phase transition directly to an ideal classical solid. Sketch the typical behavior of  $C_V$  below  $T_0$ , down to 0K, including the magnitude just below  $T_0$  and the temperature dependence just above the absolute zero temperature, and give physical justifications.
3. Given the first excited state of the rotational spectrum of this molecule is at the energy  $kT_e$  above the ground rotational state, and  $T_e = 64\text{K}$ , calculate from basic theory the rotational contribution to the specific heat capacity per molecule (in units of the Boltzmann constant  $k_B$ ) at  $T = 10\text{K}$  and  $T = 500\text{K}$ . (Note that  $T_e = 2\theta_r$ , where  $\theta_r = \frac{\hbar^2}{2Ik_B}$  is the rotational temperature, and you may make reasonable approximations in answering this part. If you don't have a calculator for the explicit evaluations, indicate what numerical expressions you would have to compute with a calculator.)

### Problem 46

A gas is described by the following equations of state

$$P = \frac{U}{3V}, \quad U = bVT^4$$

where  $b$  is a constant and  $P$ ,  $U$ ,  $V$ , and  $T$  are the thermodynamic pressure, internal energy, volume and temperature.

1. Determine the entropy  $S$  as a function of  $U$  and  $V$ .
2. Determine the functional relationship between  $P$  and  $V$  along an adiabatic path.
3. Determine the functional relationship between  $P$  and  $V$  along an isothermal path.
4. Determine the work done by the system as it expands from an initial volume  $V_0$  to a final volume  $2V_0$  along an isothermal path with temperature  $T_0$ .
5. Determine the heat added to the system as it expands from an initial volume  $V_0$  to a final volume  $2V_0$  along an isothermal path with temperature  $T_0$ .

### Problem 47 Gas of non-interacting Bose particles

Consider a gas of non-interacting Bose particles with spin  $S = 0$  and mass  $m$ . In the ultrarelativistic limit, one can approximate the dispersion relation by  $E(p) = cp$ .

1. Write down a general integral expression for the statistical average of the total number of particles not in the zero-energy ground state.
2. Determine the Bose-Einstein condensation temperature  $T_0$  of the gas as a function of the gas density  $\rho = N/V$ .
3. Determine the fraction  $N_0/N$  of the particles in the zero-energy ground state as a function of temperature  $T$  and density  $\rho$ .

You may find the following formula useful:

$$\int_0^\infty \frac{z^{x-1}}{e^z - 1} dz = \Gamma(x)\xi(x)$$

x	3/2	5/2	3	5
$\Gamma$	$\sqrt{\pi}/2$	$3\sqrt{\pi}/4$	2	24
$\xi$	2.612	1.341	1.202	1.037



### Problem 48

A chamber, that is adiabatically isolated from the outside universe, is partitioned into two volumes  $V_0$  and  $\Delta V$ . Initially the volume  $V_0$  is filled with  $N$  particles of a gas and the volume  $\Delta V$  is completely empty. The partition between the volumes  $V_0$  and  $\Delta V$  is punctured so that the gas freely expands into the additional volume  $\Delta V$  so that its final volume is  $V_0 + \Delta V$ .

1. Assuming  $\Delta V$  is small, calculate a general expression for the change in temperature  $\Delta T$ . Express your answer in terms of the following thermodynamic quantities which you can assume to be known.  
Thermal Expansion:  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$   
Isothermal Compressibility:  $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$
2. Evaluate your expression for  $\Delta T$  in the previous part for a monoatomic ideal gas.

### Problem 49

An ensemble of non-interacting pairs of Ising spins is in a magnetic field  $h$  and at temperature  $T$ . Each spin variable  $s_i^z$  can only take on values  $s_i^z \pm 1$ . The two spins within each pair interact according to the Hamiltonian

$$H = -Js_1^z s_2^z - \mu_B h (s_1^z + s_2^z), \quad \text{with } J > 0$$

1. Enumerate the possible states of a single pair and compute their corresponding energies.
2. Derive an expression for the average value of a spin,  $\langle s_i^z \rangle$ , ( $i = 1, 2$ ) as a function of  $J$ ,  $T$  and  $h$ .
3. Given the above model, determine whether there exists a temperature  $T_c$  for which  $\langle s_i^z \rangle$  can be non-zero at  $h = 0$ . Evaluate  $T$ .

### Problem 50

1. Show that the number of photons,  $N$ , in equilibrium at temperature  $T$  in a cavity of volume  $V$  is proportional to

$$V \left( \frac{k_B T}{\hbar c} \right)^3$$

2. Show that the heat capacity for this system is proportional to  $T^3$ .

### Problem 51 Stat Mech

Consider a system of non-interacting spin 1/2 fermion particles, electrons, adsorbed on a surface with specific adsorption sites. At each site, an electron can occupy any one of three distinct orbital states corresponding to energies  $\epsilon_1, \epsilon_2$ , and  $\epsilon_3$  ( $\epsilon_1 > 0, \epsilon_2 > 0$ , and  $\epsilon_3 > 0$ ). The surface is in contact with a gas of electrons that acts as a thermal and particle reservoir.

1. Determine a general expression for the average number of particles adsorbed per site if the reservoir is at a temperature  $T$  and has a chemical potential  $\mu$
2. If  $\epsilon_1 < \epsilon_2$  and  $\epsilon_2 = \epsilon_3$  within what range of values must  $\mu(T = 0)$  lie if at  $T = 0$  the average number of electrons adsorbed per site is 2.
3. If the average number of electrons adsorbed per site is maintained at 2 for small nonzero temperatures, determine the precise limiting value of  $\mu$  as  $T$  approaches zero.

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**Problem 52 Thermo**

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Consider the following equations of state for an ideal gas:

$$U = cNk_B T, \quad PV = Nk_B T$$

where  $c$  is a constant.

1. Determine the entropy as a function of  $U, V$ , and  $N$ . Let  $S = 0$  when  $U = Nu_0$ , and  $V = Nv_0$ , where constants  $u_0$  and  $v_0$  are the energy/particle and volume/particle respectively.
2. Determine the entropy as a function of  $P, T$ , and  $N$ . Let  $S = 0$  when  $T = T_0$  and  $P = P_0$ .
3. 1. If the number of particles  $N$  varies, then calculate the chemical potential in terms of  $P, T, P_0, T_0$ , and constants  $c$  and  $k_B$ .

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**Problem 53 Thermo**

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When we apply a magnetic field  $H$  to a solid body, it is permissible under many circumstances to neglect the  $-PdV$  term in comparison to the  $HdM$  term in the fundamental thermodynamic equation. Hence for a magnetizable solid body we can simply write

$$dU = TdS + HdM$$

where the magnetization  $M = \chi H$  is related to  $H$  through the susceptibility  $\chi = \chi(H, T)$ . Let  $C_H$  denote the heat capacity at constant field  $H$ ,  $C_M$  the heat capacity at constant  $M$ , and define the differential isothermal susceptibility as  $\Pi = (\partial M / \partial H)_T$ .

1. Find an expression for  $C_H - C_M$  in terms of  $T, H, \chi$ , and  $\Pi$ .
2. Show for a paramagnetic material, where  $\chi = a/T$  with  $a = \text{constant}$ , that the expression in the first part reduces to  $C_H - C_M = MH/T$ .

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**Problem 54 Stat Mech**

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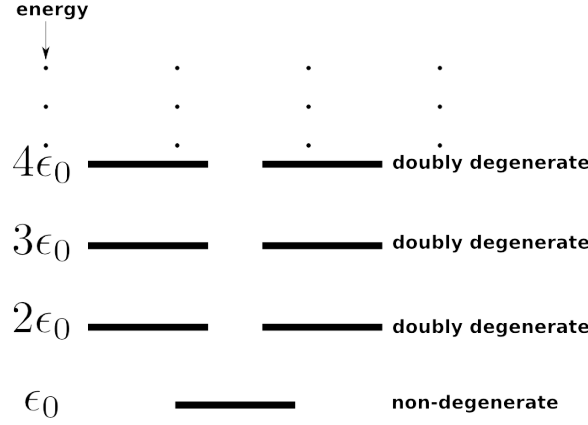
1. Shown in the figure below is a set of available single-particle states and their energies. By properly filling these single-particle states, find the energies and degeneracies for a system of four identical non-interacting particles in the system's lowest energy level and in its first excited energy level, assuming that these particles are:
  - identical spinless bosons,
  - identical spinless fermions.
2. At a finite temperature  $T$ , calculate the ratio  $r = P_1/P_0$ , again for the two cases defined above.  $P_1$  is the probability for finding the four-particle system in the first excited energy level, and  $P_0$  is the probability for finding the same system in the lowest energy level.

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**Problem 55 Thermo**

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One is given two containers. Each contains  $N$  moles of water at the same pressure. Initially the temperature of the water in each container is  $T_1$ , and  $T_2$  ( $T_2 \geq T_1$ ). The entire system is kept at a constant pressure and is thermally isolated from the surroundings. The heat capacity of water per mole,  $C_P$ , can be taken to be a constant for  $T_1 \leq T \leq T_2$ . First, consider a process when the two bodies of water are brought into thermal contact so they can exchange heat between themselves.



1. Calculate the final temperature of the resulting mixture.
2. Calculate the change in the total entropy of the two bodies of water.
3. Now, determine the theoretical maximum amount of total work that could have been obtained from this system.

### Problem 56 Thermo

During a process in which the volume of a system of  $N$  molecules is expanded from  $V_1$  to  $V_2$ , the temperature is observed to decrease linearly with the volume from  $T_1$  to  $T_2$ , that is,

$$T = T_1 + A(V - V_1)$$

where,  $A = \frac{T_2 - T_1}{V_2 - V_1}$  Express the heat transfer during this process in terms of definite integrals of

$$C_P = \frac{T}{N} \left( \frac{\partial S}{\partial T} \right)_{P,N}, \quad \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P,N}, \quad \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T,N}$$

which are assumed to be known functions of  $T$  and  $V$ .

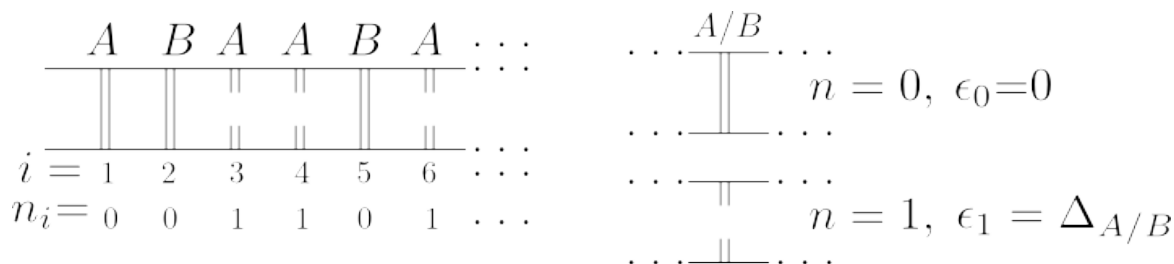
### Problem 57 Stat Mech

A simple statistical mechanical model can be used to describe thermal denaturation (strand separation) of DNA molecules. The DNA molecule is represented as a chain of two kinds of base pairs,  $N_A$  pairs of type A and  $N_B$  pairs of type B, in a given sequence. Each pair can be in two states ( $n = 0, 1$ ), either bound ( $n = 0$ ) or unbound ( $n = 1$ ), as shown in the figure. The average fraction of unbound pairs ( $f$ ) can be easily measured experimentally.

1. Sketch qualitatively, using only physical arguments,  $f$  as a function of temperature  $T$  for a pure A ( $N_B = 0$ ) and a pure B ( $N_A = 0$ ) DNA. Be sure to state the limiting values at  $T = 0$  and  $\infty$  explicitly.
2. Derive the partition function for a single DNA molecule assuming that the energy  $\epsilon_n$  of each base pair is independent of the state of other pairs, and that the unbinding energy depends only on whether the base is of type A or B,

$$\epsilon_n = \begin{cases} 0, & \text{if } n = 0 \\ \Delta_A \text{ or } \Delta_B, & \text{if } n = 1 \end{cases}$$

3. Derive a closed analytical expression for  $f$  as a function of  $T$  and  $c \equiv N_A/N$  where  $N = N_A + N_B$ .  
 [Hint: You may find the following identity useful:  $e^{-x}/(1+e^{-x}) = 1/(1+e^x) = \frac{1}{2}(1 - \tanh(x/2))$ ]
4. Using the result in the previous part and the phenomenological form  $\beta\Delta_A = a_A(T_A - T)$  and  $\beta\Delta_B = a_B(T_B - T)$ , indicate the phenomenological parameters  $a_A, a_B, T_A$  and  $T_B$  in your figures in the first part, and sketch  $f(T)$  assuming  $c = 1/4, T_B = 1.5T_A, a_A^{-1} = 0.1T_A$ , and  $a_B^{-1} = 0.1T_B$ .



### Problem 58 Stat Mech

Consider a classical system of  $N$  point particles of mass  $m$  in a volume  $V$  at temperature  $T$ . The particles interact through a two-body repulsive central potential

$$\phi(r) = \phi_0 \left( \frac{r_0}{r} \right)^n$$

where  $\phi_0 > 0, r_0 > 0$ , and  $n > 0$ .

1. Calculate the partition function  $Z(T, V)$  for this system and show explicitly that  $Z(T, V) = Z_0(T, V)q(TV^{n/3})$ , where  $Z_0$  is the ideal gas partition function and the function  $q(x)$  (which you can not express in a closed form!) depends on  $T$  and  $V$  only through  $x = TV^{n/3}$ .
2. Given the result of the previous part, show that the internal energy  $U$  and the pressure  $P$  are related as  $U = U_0 + \frac{3}{n}(P - P_0)V$ , where the subscript 0 refers to the ideal gas.
3. What is the potential  $\phi(r)$  as  $n \rightarrow \infty$ ? Explain the result obtained in the previous part in this limit. Is it correct?

### Problem 59 Thermo

A material, in a certain range of temperature  $T$  and pressure  $P$ , has a volume expansivity (or thermal expansion coefficient) given by

$$\alpha = (R/Pv) + (a/RvT^2)$$

and an isothermal compressibility given by

$$\kappa_T = [Tf(P) + (b/P)]/v$$

where  $R, a$ , and  $b$  are (non-dimensionless) constants independent of pressure  $P$  the specific volume  $v \equiv V/N$ , and the absolute temperature  $T$ , and  $f(P)$  is an unknown function of  $P$ .

1. Determine  $f(P)$ .
2. Determine  $v(P, T)$ .

## Problem 60 Stat Mech

The ground state density of a free-electron Fermi gas is conveniently parametrised by specifying the volume per conduction electron according to

$$\frac{4}{3}\pi r_s^3 \equiv \frac{V}{N}$$

1. Find the Fermi wavevector,  $k_F$  in terms of the electron density parameter  $r_s$ .
2. Find expressions for the following quantities, in terms of the dimensionless density parameter ( $r_s/a_0$ ), where  $a_0$  is the Bohr radius, and with the units indicated:
  - the Fermi momentum  $k_F$  ( in Å<sup>-1</sup> ), [Given:  $1a_0 = 0.529$  Å].
  - the Fermi energy  $\epsilon_F$  (in eV ), [Given: 1 Rydberg = 13.6 eV ]
  - the Fermi temperature  $T_F$  (in K). [Given: 1 eV =  $k_B \times 1.16 \times 10^4$  K.]

In each case, a detailed expression for the coefficient involved should be found so that if you had a calculator you would be able to evaluate the coefficient numerically.

3. Starting from the equation of state

$$PV = \frac{2}{3}\langle E \rangle$$

where  $\epsilon_F$  is the total internal energy of the gas, express the  $T = 0$  value of the bulk modulus

$$B \equiv -V \left( \frac{\partial P}{\partial V} \right)_{T,N}$$

which is the inverse of the isothermal compressibility  $\kappa_T \equiv -\frac{1}{V}(\partial V/\partial P)_{T,N}$  in terms of the Fermi energy  $\epsilon_F$  and the density parameter  $r_s$ .

## Problem 61 Thermo

Using some simple reasoning, obtain the functional dependencies of the low- and high- temperature behaviors (i.e., for  $T \ll \epsilon_F$  and  $T \gg \epsilon_F$ ) of the following quantities for a three-dimensional ideal Fermi gas, in terms of  $N$  (the total number of particles),  $T$  (the absolute temperature),  $\epsilon_F$  (the Fermi energy), and  $k_B$  (the Boltzmann constant):

1. the total specific heat at a constant volume  $C_V$ ,
2. the total entropy  $S$ ,
3. the total internal energy  $E$ . In each expression, you may introduce any number of undetermined numerical constants, but not any un-determined dimensional quantities. For each of the three physical quantities listed above, draw also a qualitative sketch of its  $T$ -dependence from  $T = 0$  up to a temperature  $T \gg \epsilon_F$ , based on the low- and high-temperature behaviors of it you have deduced.

## Problem 62 Thermo

Over some range of parameters a system is described by the following fundamental equation:

$$S = Au^{1/3}v^{1/3}$$

where  $s$ ,  $u$ , and  $v$  are the molar entropy, molar energy, and molar volume, respectively and  $A$  is a constant.  $N$  moles of this fluid is initially confined to a volume  $V_i$  at pressure  $P_i$ . It then expands reversibly at constant temperature  $T_0$  to a final volume  $V_f > V_i$ .

1. Determine the final pressure  $P_f$  in terms of  $V_i, V_f$ , and  $P_i$ .
2. Determine an expression for either the chemical potential  $\mu$  or an expression for the change in chemical potential,  $d\mu$ , and explain whether the chemical potential of this system increases or decreases for this process?

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### Problem 63 Thermo

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For a system in an electric field  $E$  the differential of the internal energy is

$$dU = TdS + Ed\Pi$$

where  $\Pi$  is the electric polarization of the system. Define the generalized Helmholtz free energy  $F(T, \Pi)$ , the generalized enthalpy  $H(S, E)$  and the generalized Gibbs free energy  $G(T, E)$  for this system in terms of the variables  $T, S, E$ , and  $\Pi$ . Write the differentials for these thermodynamic functions and use these to find the four Maxwell relations between derivatives of these variables. (Note: for this particular system the pressure  $P$  and volume  $V$  are not relevant variables, so don't include them in your work.)

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### Problem 64 Stat Mech

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For an isotropic three-dimensional solid whose velocity of sound  $c$  is the same for all three modes, find the expression for the Debye temperature  $\theta_D$  (where  $\hbar\omega_{max} = k_B\theta_D$ ). Show that the number of phonons exceed in this solid is proportional to  $T^3$  for  $T \ll \theta_D$  and proportional to  $T$  for  $T \gg \theta_D$ .

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### Problem 65 Thermo

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The figure shows the pressure versus molar volume isotherms for the Van der Waals gas

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

1. Which of the isotherms in the figure contains regions that do not satisfy the thermodynamic stability conditions?
2. Which isotherm represents the critical temperature?
3. Sketch on the graph the region in which the system is unstable to local perturbations (spinodal line).
4. Sketch on the graph the region in which the system is globally unstable.
5. What is physically occurring within this region of global instabilities?
6. Sketch the qualitative behavior of the molar volume against temperature for an isobar at  $P = 0.02$  and  $P = 0.06$ .

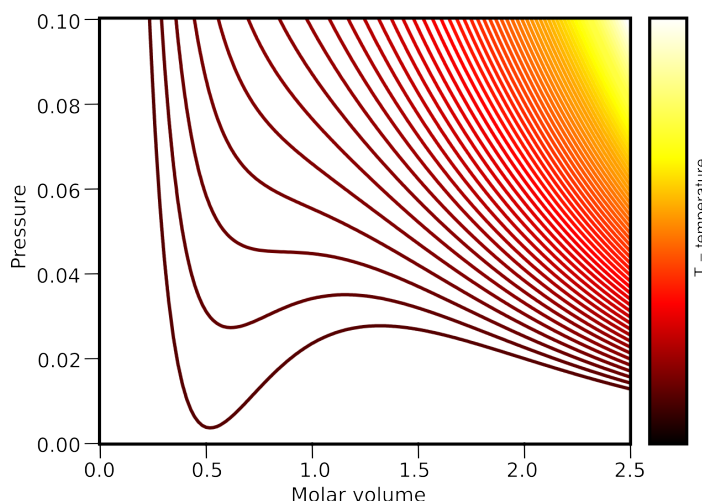
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### Problem 66 Thermo

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An ideal gas is expanded adiabatically from  $(P_1, V_1)$  to  $(P_2, V_2)$  [AB in figure below]. Then it is compressed at constant pressure to  $(P_2, V_1)$  [BC]. Finally the pressure is increased to  $P_1$  at constant volume  $V_1$  [CA].

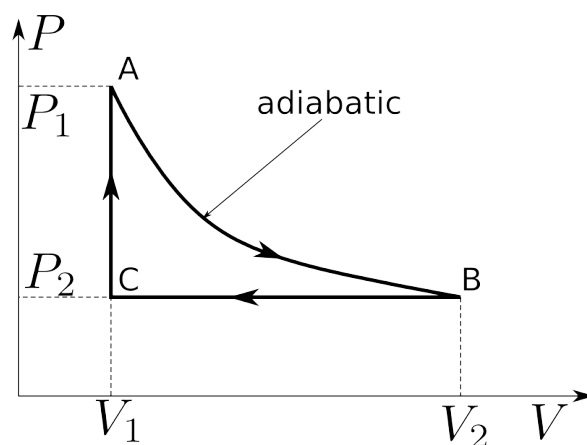
1. Calculate  $W_{BC}$ , the work done by gas in going from B to C.
2. Calculate  $W_{CA}$ , the work done by gas in going from C to A.



3. For an ideal gas, show that  $C_P = C_V + Nk$ , and hence that  $C_V = Nk/(\gamma - 1)$ , where  $\gamma \equiv C_P/C_V$ . (Here  $N$  is the number of molecules and  $k$  is the Boltzmann constant. )
4. Calculate  $W_{AB}$  the work done by gas in going from A to B, in terms of  $\gamma$ ,  $P_2$ ,  $V_2$ ,  $P_1$ , and  $V_1$
5. Calculate  $Q_{CA}$ , the heat absorbed by gas in going from C to A, in terms of  $\gamma$ ,  $V_1$ ,  $V_2$ ,  $P_2$  and  $P_1$ .
6. Calculate the efficiency  $\eta \equiv W/Q_{CA}$  of the engine, and show that it is given by

$$\eta = 1 - \gamma \frac{1 - V_2/V_1}{1 - P_1/P_2}$$

(Why do you need to divide by  $Q_{CA}$  and not by  $Q_{CA} + Q_{BC}$  ?)



## Problem 67 Thermo

Molecules do not all pile up at the bottom of the atmosphere, but rather have a density  $n$  that decreases as one moves higher in the atmosphere. The pull of gravity is countered by upward diffusion. Consider a monoatomic gas of molecules of mass  $m$ , in a uniform downward gravitational field  $g$ . Take the  $y$ -direction to be upward.

1. Using  $N$  as the number of molecules in a gas,  $V$  as its volume, and  $k_B$  as the Boltzmann constant, write down the ideal gas law.

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- Find the differential equation for the pressure  $P(y)$  under gravity by finding the equilibrium condition for the matter in a slab of area  $A$  and thickness  $dy$ .
  - For an isothermal atmosphere if  $P = P_0$  at  $y = 0$ , find  $P(y)$ .
  - Find the density  $n(y)$ .
  - If the drift velocity due to gravity is  $v = \mu mg$ , where  $\mu$  is called the mobility, write down the number current density  $J_g$  due to the pull of gravity, including its direction.
  - The number current density due to diffusion is  $J_{diff} = -D\partial_y n$ , where  $D$  is called the diffusion constant. Setting to zero the sum of the number current densities due to gravity and due to diffusion, find a relationship between  $D$  and  $\mu$ .

### Problem 68 Stat Mech

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Consider a set of  $N$  indistinguishable spin-1 objects, each with energy

$$E = AS_z + BS_z^2$$

where  $S_z$  is given in units where  $\hbar = 1$ . Thus  $A$  and  $B$  are energies.

- With  $(n_1, n_0, n_{-1})$  the numbers of spins in the states with  $S_z = 1, 0, -1$  respectively, find the number of arrangements  $W$  of the spins that will produce these numbers.
- Write down the free energy  $F$  for this system, in terms of  $n_1, n_0, n_{-1}$  the temperature  $T$ , and  $N$ . Use  $\log(m!) = m \log(m) - m$  for large  $m$ . Set  $k_B = 1$ .
- Using  $n_1$  and  $n_0$  as independent variables, minimize  $F$  to find  $n_1, n_0$ , and  $n_{-1}$ , in equilibrium at a given temperature  $T$ .

### Problem 69 Stat Mech

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Consider a one-dimensional (non-harmonic) oscillator with energy given by

$$E = \frac{p^2}{2m} + bx^4$$

where  $p$  is the momentum and  $b$  is some constant. Suppose this oscillator is in thermal equilibrium with a heat bath at a sufficiently high temperature  $T$  so that classical mechanics is valid.

- Compute its mean kinetic energy as a fraction of  $kT$ .
- Compute its mean potential energy as a fraction of  $kT$ .
- Consider a collection of such non-interacting oscillators all at thermal equilibrium in one-dimension. What is the specific heat (per particle) of this system?

[Hint: You might use

$$\int_0^\infty x^{n-1} e^{-x} dx = \Gamma(n), \quad n \neq -1, -2, \dots$$

or an integration by parts in solving this problem.]



### Problem 70 Thermo

The equation of state for an ideal gas is  $PV = nRT$

1. Prove that the internal energy  $U(V,T)$  is a function of  $T$  only.
2. If the entropy at  $T_0, V_0$  is  $S_0$ , find the entropy at any other  $T, V$  assuming the molar specific heat  $CV$  is a given constant. (Express the answer for  $S$  as a function of the variables  $T, V$ .)
3. Show that the reversible work done in an isothermal expansion is equal to the negative of the change in free energy.

### Problem 71 Stat Mech

1. Determine the chemical potential, at temperature  $T = 0$  and at number density  $n$  for a non-interacting, non-relativistic Fermi gas of spin-1/2 and mass  $m$  ( $\epsilon = p^2/2m$ )
2. Repeat the previous part for the relativistic case ( $\epsilon = cp$ )
3. Show that, at some critical density  $n$ , and  $T = 0$ , the proton-electron plasma starts a transition into the degenerate neutron gas. Neglect any interaction between the particles and consider the electron and proton systems as Fermi gases. Take into account the mass difference  $\Delta M$  between the neutron and proton. Since  $m_e \ll \Delta M$ , the electrons must be treated relativistically. Assume that neutrons created in the course of this transformation leave the system. Neglect gravity.
4. Consider such a system in a box of volume  $V$ , with  $n < n_c$ . Determine the number of electrons  $N_e$  and their pressure as the volume is decreased somewhat below the volume where the transition occurs. Do not consider compression so high that complete conversion occurs.

### Problem 72 Stat Mech

The 1-dimensional Ising model is defined as a chain with "spins"  $\sigma_n$ , on each site  $n$  ( $n = 1, 2, \dots, N$ ) independently taking one of two values  $\sigma_n = \pm 1$ . The energy of this system can be written as follows:

$$H = -J \sum_{n=1}^{N-1} \sigma_n \sigma_{n+1}$$

where  $J$  is a positive constant.

1. Introduce "spins on a bond"  $\tau_n = \sigma_n \sigma_{n+1}$  as new variables. Explain why the  $\tau$ 's are independent. Find the partition function.
2. Find the free energy and the heat capacity per site.
3. Find the asymptotic behavior of the heat capacity at  $T \ll J$  and at  $T \gg J$ . Give a physical explanation for the dominant behavior at  $T \ll J$ .

### Problem 73 Thermo

The total entropy  $S$  for a system of  $N$  particles in a container of volume  $V$ , with total energy  $E$ , is

$$S = aE^{1/3}V^{1/3}N^{1/3}$$

where  $a$  is a constant.

- 
1. Compute the temperature, pressure, and chemical potential as functions of  $S$ ,  $V$ , and  $N$ .
  2. Stability, the Third Law, and the extensivity property provide some constraints on allowable thermodynamic quantities (Extensivity refers to how various quantities scale when two identical systems are combined.) Discuss how the results from the previous part satisfy or do not satisfy these constraints.
  3. Compute the Helmholtz free energy  $F(T, V, N)$ , and from  $F$  compute  $S(T, V, N)$ . Show that this is consistent with the entropy  $S(E, V, N)$  given initially.

### Problem 74 Thermo

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Consider a cylinder of water that undergoes a slow adiabatic compression

1. What thermodynamic property of the water will be constant during an adiabatic compression? Use this to write a simple equation connecting small temperature changes,  $\Delta T$ , to pressure changes,  $\Delta P$ , to first order.
2. The temperature change in an adiabatic compression can be related to the water's compressibility,  $\alpha \equiv \frac{1}{V}(\partial V/\partial T)_P$ , and its specific heat at constant pressure,  $C_P$ . To do so, first find a Maxwell relation which will connect the compressibility to a derivative of the entropy.
3. Now transform your equation from the first part, in order to express small temperature changes,  $\Delta T$ , to adiabatic pressure changes,  $\Delta P$ , in terms of the temperature, volume,  $C_P$ , and the compressibility. Consider  $\alpha$ , and  $C_P$ , to be essentially constant during the process.

### Problem 75 Thermo

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Specific heat of a gas-liquid system:

1. What general expression relates pressure and temperature changes for condensation and evaporation along an equilibrium liquid-gas coexistent curve?
2. Consider a liquid and its vapor, and assume that the vapor behaves as an ideal gas. Express the slope  $(\partial P/\partial T)$  along the coexistence curve, in terms of the latent heat of vaporization ( $L_v$ ) of the system, plus other thermodynamic quantities.
3. Now find an expression for the specific heat of the gas, following the coexistence curve (that is, the specific heat calculated from the heat into the gas only, as it contacts the liquid), in terms of  $T$ , ( $L_v$ ), and the specific heat at constant pressure ( $C_P$ ).  $C_P$ , (assumed to apply only to the gas) and  $L_v$  may be taken to be constant. [Hint: a Maxwell relation may be used to obtain the final answer.]
4. Show from your result that there is a temperature regime in which the specific heat of the gas is negative. Does this mean that the gas is thermodynamically unstable?

### Problem 76 Thermo

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Consider a classical gas, in equilibrium at temperature  $T$ , with no interactions between gas particles. Each particle has mass  $m$ .

1. Write down the general form of the velocity (not speed) distribution function for such a gas. This should be a probability function per unit volume, per  $d^3\vec{v}$ . Assume the gas as a whole is at rest in your coordinate system. Determine the normalizing constant.

2. Obtain  $v_{\text{rms}}$ , which is the root-mean-square velocity for this gas, using your distribution function (You get credit for demonstrating the method, not for recalling the result.)
3. Find the probability that a gas particle will have a positive  $x$  velocity component that exceeds  $v_{\text{rms}}$ . (There is a table of values in the CRC tables that can be used to evaluate the integral.)

### Problem 77 Stat Mech

In so-called intrinsic semiconductors at  $T = 0$ , electrons fill the lower (valence) band, whereas the upper (conducting) band is empty. Let the maximal energy of the valence band and the minimal energy of the conducting band correspond to the momentum  $\vec{p} = 0$  and be separated by the energy gap  $E_g$ . Assume that near the minimum (maximum) the energy  $\epsilon(p)$  can be represented approximately by an expansion:

$$\epsilon_c = \frac{E_g}{2} + \frac{p^2}{2m_c}; \quad \epsilon_v = -\frac{E_g}{2} - \frac{p^2}{2m_v}$$

where  $E_g$  is the gap in the electron spectrum and  $m_c, m_v$  are effective masses of electrons and holes respectively.

1. Using the electro-neutrality condition, (i.e., the number of thermally excited holes in the valence band equals the number of thermally excited electrons in the conduction band.), calculate the chemical potential  $\mu$  for electrons as a function of temperature at a temperature  $T \ll E_g$ .
2. Calculate the density of electrons in the conducting band and the density of holes in the valence band at a temperature  $T \ll E_g$ .

### Problem 78 Stat Mech

Calculate the efficiency of a Stirling engine using a classical ideal gas. In the Stirling engine the gas is compressed isothermally from a volume  $V_1$  to a smaller volume  $V_2$  at a temperature  $T_2$  then it is heated at a fixed volume  $V_2$  to a higher temperature  $T_1$ ; then it performs work, expanding isothermally to the initial volume  $V_1$ , and finally it returns to the initial temperature  $T_2$  by cooling at fixed volume  $V_1$ .

### Problem 79 Stat Mech

A 2-dimensional classical ideal gas of  $N$  particles at a temperature  $T$ , is contained to an area  $A$  in the  $x - y$  plane.

1. Find the partition function and the free energy for this system.
2. Determine the surface tension as a function of temperature and density (number of particles per unit area)  $n = N/A$
3. If the same gas is placed in a field of constant force per particle,  $F$ , directed along the  $x$ -axis, determine the density  $n$  as a function of  $x$ .
4. Find how the surface tension varies with  $x$ .

### Problem 80 Stat Mech

Consider a solid with  $N$  atoms each having a mass  $m$ . Assume that each atom has three independent modes of oscillation, each at the same frequency  $\omega_0$ . This is known as the Einstein model. Let the solid be in equilibrium with a vapor of the same type of atom, and let  $\epsilon_0 > 0$  be the sublimation energy per

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atom, i.e. the energy which is necessary to remove an atom from the solid to the vapor with zero final kinetic energy.

The vapor can be treated as an ideal gas. Its free energy is

$$F_g = -k_B T N_g \left[ \log \left( \frac{V_g}{N_g \Lambda_T^3} \right) + 1 \right], \quad \Lambda_T = \frac{\sqrt{2\pi\hbar}}{\sqrt{mT}}$$

where we have assumed that the vapor contains  $N_g$  particles occupying a volume  $V_g$ .

1. Find the free energy  $F_s$  of the solid.
2. Find the equilibrium vapor pressure as a function of temperature if the volume  $V_g$  is maintained constant. Neglect any volume changes in the solid, due to evaporation.

### Problem 81 Stat Mech

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The surface of the sun has the temperature 6000K. The sun's radius is  $R \approx 10^6$  km

1. Assuming that the sun is a black body, what is the emitted power per cycle  $d\mathcal{P}/df$  at a wavelength of 3cm? (Please give a simple approximate expression.)
2. What is the emitted power per cycle  $d\mathcal{P}/df$  at the wave-length  $3 \times 10^{-6}$  cm ?
3. Indicate how you would determine the power  $\mathcal{P}$  integrated over all frequencies.

### Problem 82 Thermo

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One mole of an ideal gas, with internal energy  $U = \frac{5}{2}nRT$  ( $n = 1$  mole), is taken from an initial state i, with pressure  $P_0$  and volume  $V_0$  to a final state  $f$  with  $P_f = 2P_0$  and  $V_f = 2V_0$  by two different paths:

Path 1: The gas undergoes an isothermal expansion from  $V_0$  to  $2V_0$ , and then the pressure is increased to its final value  $P_f$  at constant volume.

Path 2: The gas undergoes an isothermal compression to  $P_f$ , and then is expanded at constant pressure to its final volume  $V_f$ .

1. Sketch  $P - V$  diagrams for each case.
2. Find the heat  $Q$  added to the system in each step of the above two processes in terms of  $P_0, V_0$ , and other constants.
3. Find the change in entropy of the gas in going from the initial to the final state.

### Problem 83 Thermo

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The cycle of a highly idealized gasoline engine can be approximated by the Otto cycle. Steps  $1 \rightarrow 2$  and  $3 \rightarrow 4$  are adiabatic compression and expansion, respectively. Steps  $2 \rightarrow 3$  and  $4 \rightarrow 1$  are isochoric (constant volume) processes. Treat the working medium as an ideal gas with constant  $\gamma = C_P/C_V = 5/3$  and take  $V_1 = 3V_2$ ,  $P_1 = 1 \text{ atm}$  ( $10^5 \text{ N/m}^2$ ), and  $P_3 = 2P_2$ .

1. Sketch the cycle on a  $P - V$  diagram.
2. Compute the efficiency of this cycle for compression ratio  $r = V_1/V_2 = 4$ .
3. Calculate the work done on the gas during the two steps  $1 \rightarrow 2$  and  $2 \rightarrow 3$ .
4. Calculate the entropy changes of the gas during the two steps  $1 \rightarrow 2$  and  $2 \rightarrow 3$ .

### Problem 84 Stat Mech

A cylindrical container of height  $L$  and radius  $R$  contains many identical non-interacting particles of mass  $m$  at temperature  $T$ . If the container rotates about its axis at angular velocity  $\omega$ , the single-particle Hamiltonian in the rotating frame is given by

$$H = \frac{p^2}{2m} - \frac{m\omega^2 r^2}{2}$$

where  $r$  is the radial coordinate, and  $p$  is the total momentum.

1. The earth's atmosphere thins out with increasing height, because of gravity. A similar effect occurs for the gas within this rotating container. Determine how the pressure and density vary with radial coordinate  $r$ .
2. If the system has  $N$  particles, obtain the density as a function of  $r$ .
3. Obtain an approximate expression for the density distribution at high rates of rotation, i.e,  $m\omega^2 R^2/2 \gg k_B T$ . In this case, essentially all of the gas is compressed into a region of characteristic thickness  $d < R$  close to the wall. How does  $d$  scale with  $m, \omega$ , and  $T$ ? For hydrogen molecules at room temperature, in a container with  $R = 5\text{cm}$ , estimate the numerical value of  $\omega$  where  $d$  equals  $0.1R$ .

Boltzmann constant  $k_B = 1.38 \times 10^{-23} \text{J/K}$

Speed of light  $c = 3.0 \times 10^8 \text{m/s}$

Proton mass  $m_p = 1.67 \times 10^{-27} \text{kg}$

### Problem 85 Topic

A horizontal wire of length  $L$  is fixed at both ends and tightened to a tension  $F$ . It is in equilibrium with a heat bath at temperature  $T$ .

1. Because of thermal fluctuation, the midpoint of the wire is sometimes displaced vertically by a distance  $y$  ( $y \ll L$ ). Find the work done by the heat bath to the wire.
2. Find the probability for such displacement to happen.
3. Find the root-mean-square displacement of the midpoint of the wire.

### Problem 86 Topic

In a "hot quark-gluon plasma", the gluons are massless spin-1 particles (energy-momentum relation  $\epsilon = cp$ ), with eight degenerate "colors", and quarks are relativistic spin-1/2 particles with three degenerate "colors" and two degenerate "flavors".

1. Determine the degeneracy factors  $d_G$  and  $d_C$  for the gluons and the quarks. In what follows, consider only the gluons, and take volume  $V$ .
2. Determine the thermal average for the total energy  $E$  for the gluons. (Gluons are not conserved; from this one can show that their chemical potential  $\mu_G = 0$ .) Leave any integrals in dimensionless form; do not evaluate them.
3. Determine the heat capacity  $C_V$ , and the entropy  $S$ .
4. Determine the free energy  $F$  and the pressure  $P$  associated with the gluons. Show that  $P = \frac{1}{3}E/V$

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**Problem 87 Topic**

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Consider a crystal with  $p$  identical hydrogen atoms distributed over  $J$  identical bulk sites and  $K$  identical surface sites. Let  $p \ll J$ . The atoms do not interact, but they have an energy  $\epsilon_B$  at the bulk sites, and an energy  $\epsilon_S$  at the surface sites. Let  $b$  be the number of atoms at bulk sites, and let  $s$  be the number of atoms at surface sites, so  $p = b + s$ .

1. If  $\epsilon_B = \epsilon_S$ , what is the ratio  $b/s$  at all temperatures? Explain your reasoning. In what follows, do not assume that  $\epsilon_B = \epsilon_S$ .
2. Find the number of ways  $W(J, b)$  that  $b$  atoms can be distributed over the  $J$  bulk sites. Find the bulk entropy  $S_B(J, b)$ , the bulk energy  $E_B(J, b)$ , and the bulk free energy  $F_B(T, J, b)$ .
3. Find the number of ways  $W(K, s)$  that  $s$  atoms can be distributed over the  $K$  surface sites. Find the surface entropy  $S_S(K, s)$ , the surface energy  $E_S(K, s)$  and the surface free energy  $F_S(T, K, s)$ .
4. Minimize the total free energy  $F_B(T, J, b) + F_S(T, K, s)$  with respect to  $b$  at fixed  $b + s = p$ . Find  $b/s$  for  $p \ll J, K$ . Note that, for large integer  $z$ ,  $\ln(n!) = z \ln(z) - z$ .
5. Find  $b/s$  in the following limits: at high  $T$ ; at low  $T$  if  $\epsilon_S \ll \epsilon_B$ ; at low  $T$  if  $\epsilon_S \gg \epsilon_B$ .

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**Problem 88 Topic**

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A set of  $N$  non-interacting molecules are fixed in space. Each has a permanent electric dipole moment of magnitude  $p_0$  that is free to rotate in three dimensions. They are in a uniform electric field  $\vec{E} = E_0 \hat{z}$ .

1. Find the thermal average, at temperature  $T$ , of their total electric dipole moment  $\vec{P}$ .
2. Evaluate  $\vec{P}$  at low  $T$ , and explain your result physically. Define 'low  $T$ ' in terms of the parameters of the problem.
3. Evaluate  $\vec{P}$  at high  $T$ .
4. At 'high'  $T$  find the electric polarizability  $\alpha = \partial P / \partial E$ , taking  $\vec{P}$  and  $\vec{E}$  along  $\hat{z}$ .

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**Problem 89 Topic**

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Find the entropy rise  $\Delta S$  of a monoatomic ideal gas of  $N$  molecules occupying the volume  $V_1$  when it expands to a volume  $V_2$  under constant pressure.

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**Problem 90 Topic**

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1. Using the extensivity/intensivity properties of the thermodynamic quantities, show that  $U = ST - PV + \mu N$ .
2. Using this result, prove the following thermodynamic identity:

$$\frac{1}{n^2} \left( \frac{\partial n}{\partial \mu} \right)_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{N, T}$$

where  $-V^{-1}(\partial V / \partial P)_{T, N}$  is the isothermal compressibility and  $n = N/V$  is the particle number density. Here  $P$  denotes the pressure,  $T$  the absolute temperature, and  $\mu$  the chemical potential.

**Problem 91 Topic**

Consider a two-dimensional ideal neutron gas with areal number density ( i.e., number per unit area)  $n$  at temperature  $T$  and zero magnetic field. Each neutron has a mass  $m$ .

1. Derive a closed-form expression for the chemical potential  $\mu$  as a function of  $T$  and  $n$ .
2. A magnetic field  $H$  is now applied to the system. Each neutron has a magnetic moment  $\mu_N$  whose direction is opposite to its spin. Derive a relation which gives implicitly the function  $\mu(T, n, H)$ . Use this relation to show that  $(\partial\mu/\partial H)_{T,n|H=0} = 0$ .
3. Derive a closed-form expression for the zero-fold spin-susceptibility  $\chi_S \equiv (\partial M/\partial H)_{T,n|H=0}$  of the system as a function of  $T$  and  $n$ . Note, that the definition of  $\chi_S$  has  $n$  kept constant and not  $\mu$ , so you must properly use the result of the previous part to do this part correctly.

**Problem 92 Topic**

You should express your answers for this problem in terms of any of the following

Temperature	$T$
Volume	$V$
Pressure	$P$
Heat Capacity at constant volume	$C_v$
Isothermal Compressibility	$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$
Thermal Expansion	$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$

1. Express the incremental heat  $\delta Q$  absorbed by a gas if the pressure of the gas is increased incrementally from  $P$  to  $P + \delta P$  while maintaining a fixed volume.
2. For the same process, determine the incremental change in the enthalpy of the gas,  $\delta H$  where  $H = U + PV$ .
3. Evaluate your answers in for the first and the second parts for the case of an ideal monoatomic gas.

**Problem 93 Topic**

It is given that the equation of state of a certain photon-like gas is given by

$$P = a\epsilon(T)$$

where  $P$  denotes pressure,  $a > 0$  is a constant, and  $\epsilon(T)$  is the internal energy per unit volume of the photon gas at temperature  $T$ .

1. Calculate the temperature dependence of the total internal energy  $U$  for the whole gas using the equation

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

One unknown constant is allowed to appear in your answer, but no unknown functions of either  $T$  or  $V$  or both are allowed to appear.

2. Calculate the entropy  $S$  of the system as a function of  $T$  and  $V$ .

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[Hint: Start from the equation

$$dS = \frac{1}{T}(dU + PdV) = \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] dV$$

evaluate  $(\partial S/\partial T)_V$ , and  $(\partial S/\partial V)_T$ , and then integrate them to obtain S. Use the third law of thermodynamics to fix any unknown integration constant(s) of this step.]

### Problem 94 Topic

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A molecule has energy  $E = \frac{1}{2}mv^2 + \lambda j$ , where  $v$  is the velocity,  $\lambda$  is a constant with the dimension of energy, and  $j$  is an internal quantum number which can take all odd integer values (no degeneracy). It is in a cubic box of volume  $V$  with its walls maintained at the absolute temperature  $T$ .

1. Calculate the average energy of the molecule as a function of  $T$  assuming that it is in thermodynamic equilibrium with the walls of the box.
2. Calculate the free energy of the molecule as a function of  $T$ .
3. Calculate the entropy  $S$  of the molecule as a function of  $T$ .

### Problem 95 Topic

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In thermodynamics, all physical properties can be calculated once one of the thermodynamic potentials is known as a function of appropriate variables (e.g.  $U(S, V, N)$ ). Unfortunately, the thermodynamic potentials can not be directly measured but need to be calculated from experimentally accessible quantities, such as the specific heat at a constant volume  $c_v = T(\partial s/\partial T)_v$ , the isothermal compressibility  $\kappa_T = -v^{-1}(\partial v/\partial P)_T$  and the thermal expansion coefficient at constant pressure  $\alpha = v^{-1}(\partial v/\partial T)_P$ , where  $N$  is the particle number,  $P$  is the pressure,  $T$  is the temperature,  $s = S/N$  is the specific entropy and  $v = V/N$  is the specific volume.

Given the following values for these quantities:

$$c_v = \frac{4v_0 P_0 T}{T_0^2} \left( \frac{v}{v_0} \right)^{1/2}, \quad \kappa_T = \frac{2}{P}, \quad \alpha = \frac{4}{T}$$

and that the pressure, specific volume and temperature are all known at a particular reference state (i.e.,  $P_0$ ,  $v_0$ , and  $T_0$ ), determine

1. The specific volume as a function of  $T$  and  $P$  and the constants of the reference state,  $P_0$ ,  $v_0$ , and  $T_0$ .
2. The specific entropy as a function of  $T$  and  $P$  and the constants of the reference state,  $P_0$ ,  $v_0$ , and  $T_0$ . (You may assume that the third law of thermodynamics is valid for this system, and use it to fix an integration constant.) [Hint: First obtain  $S(T, v)$  and then convert it to  $S(T, P)$ ].
3. The specific Gibbs free energy  $g$  as a function of  $T$  and  $P$  and the constants of the reference state,  $P_0$ ,  $v_0$ ,  $T_0$ , and  $g_0$ .

### Problem 96 Topic

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The fundamental thermodynamic relation for a rubber band is

$$dU = TdS + \tau dl$$

where  $U$  is the internal energy,  $T$  is the absolute temperature,  $S$  is the entropy,  $T$  is the tension and  $l$  is the length of the rubber band.



1. What is  $dH$ , where the generalized enthalpy for this system is  $H = U - \tau l$ .
2. Derive the Maxwell relation that is associated with the expression for  $dH$ . State clearly what variable is held constant in each partial derivative.
3. Using the known fact that a rubber band contracts when it is heated at constant tension, deduce from the Maxwell relation obtained in the previous part that a rubber band warms when it is stretched adiabatically.

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**Problem 97 Topic**

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Consider a classical ideal monoatomic gas at temperature  $T$  in a uniform gravitational field (i.e., an isothermal atmosphere). Assume that the gas atoms have mass,  $m$ , and that their distribution over all possible heights from  $z = 0$  (the surface of the earth) to  $z = \infty$  is an equilibrium one. Denote the magnitude of the gravitational acceleration by  $g$  and assume that it can be taken to be a constant for all values of  $z$ .

1. Find the probability density governing the fraction of atoms per unit height at a height  $z$ .
2. Find the mean potential energy per atom.
3. Find the total internal energy and total heat capacity of the gas (i.e., the total amount of heat energy required to increase the temperature of the entire gas column by 1K).

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**Problem 98 Topic**

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The intersection of two Gibbs free energy surfaces is a line where  $G_\alpha = G_\beta$ , along which two phases  $\alpha$  and  $\beta$  coexist. Let the phases  $\alpha$  and  $\beta$  be the liquid phase and the gas phase, respectively. Along the liquid-gas coexistence line in the  $P - T$  plane, show that, to a very good approximation,

$$\log \left( \frac{P}{P_0} \right) = \frac{L_{vap}}{R} \left( \frac{1}{T_b} - \frac{1}{T} \right)$$

where  $P$  is the vapor pressure of the liquid present,  $P_0$  is the atmospheric pressure (1atm),  $R$  is the ideal gas constant,  $T$  is the absolute temperature,  $T_b$  is the boiling point of the system (at atmospheric pressure), and  $L_{vap}$  is the heat of vaporization per mole (whose dependence on  $T$  and  $P$  may be neglected). You may assume that the gas phase obeys the ideal gas law.

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**Problem 99 Topic**

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You are given two objects with the same total heat capacity,  $C_0$  which is temperature independent. (These objects are finite and should not be treated as thermal reservoirs.) The two objects are initially at temperatures  $T_1$  and  $T_2$  ( $T_1 > T_2$ ) respectively.

1. What type of heat engine would you operate between these two objects so that the maximum total amount of useable work is extracted?
2. Using this type of heat engine, determine the final temperatures of the two objects.
3. Using this type of heat engine, determine the total amount of useable work extracted.

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**Problem 100 Topic**

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According to the principles of quantum statistical mechanics, the pressure of black-body radiation inside a volume  $V$  may be calculated by treating the radiation as a photon gas, and using the relation

$$\bar{p} = \frac{1}{\beta} \frac{\partial \log Z}{\partial V}$$

where  $\bar{p}$  is the mean pressure,  $Z$  the partition function, and  $\beta = 1/k_B T$  is kept constant. You may assume that the volume  $V$  is a cubic box of edge length  $L = V^{1/3}$ , with walls maintained at temperature  $T$ .

1. Express the partition function  $Z$  in terms of the energies  $\epsilon_s$ , of a set of independent photon states (i.e., normal modes) in the volume, and use it to show that

$$\bar{p} = - \sum_s \frac{\partial \epsilon_s}{\partial V} \bar{n}_s$$

where  $n_s$  is the mean population of the state  $s$  with energy  $\epsilon_s$ .

2. Using the above result, obtain an explicit relation between the mean pressure  $\bar{p}$  and the mean energy density  $\bar{u}(= \bar{E}/V)$  of the photon gas.

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**Problem 101 (Thermodynamic relations)**

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Let

$$F = -A \frac{N^2}{V} T - \frac{1}{2} B \frac{N^3}{V^2} T^2 - CN$$

describe the Helmholtz free energy of a system of  $N$  particles in a volume  $V$  at temperature  $T$ , for a finite interval of temperature not including absolute zero. Here  $A$ ,  $B$ , and  $C$  are positive constants.

1. Find  $S$ ,  $P$ , and  $\mu$  in terms of  $N$ ,  $V$ , and  $T$ , where  $S$  is the total entropy,  $P$  is pressure, and  $\mu$  is the chemical potential.
2. Find the energy  $U$  in terms of  $N$ ,  $V$ , and  $S$ .
3. Find  $T$  in terms of  $N$ ,  $V$ , and  $S$ , and verify that it is consistent with the results of the first part.
4. Find the isothermal compressibility  $\kappa_T = -V^{-1}(\partial V/\partial P)_{T,N}$ .
5. Find the total heat capacity  $C_V$ .

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**Problem 102 (...)**

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It is given that

$$\begin{aligned} N(T, V, z) &= VT^3 f_1(z) \\ U(T, V, z) &= VT^4 f_2(z) \end{aligned}$$

where  $N$  is the total particle number,  $U$  is the total internal energy,  $T$  is the absolute temperature,  $V$  is the total volume of the system, and  $z \equiv e^{\beta\mu}$  is the fugacity, with  $\beta = 1/k_B T$ , and  $\mu$  the chemical potential. Let  $C_V \equiv (\partial U/\partial T)_{V,N}$  denote the total heat capacity of the system at constant volume, and  $C_V$  in terms of  $T$ ,  $V$ ,  $f_1(z)$ ,  $f_2(z)$ , and the derivatives of  $f_1(z)$  and  $f_2(z)$ .

I don't see a question here! Should we delete this one? -Ben

**Problem 103 (Thermodynamic relations)**

Consider a system of  $N$  independent harmonic oscillators with the same frequency  $\omega$ . The system is at temperature  $T$ .

1. Show that the partition function of the system is

$$Q_N = \left[ 2 \sinh \left( \frac{\hbar\omega}{2k_B T} \right) \right]^{-N}$$

2. Using this result, obtain the internal energy  $U$  of the system as a function of  $T$  and  $N$ .
3. Show that the heat capacity is

$$C = Nk_B \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \left( \frac{\hbar\omega}{k_B T} \right)^2$$

and it approaches to 0 as  $T \rightarrow 0$ .

4. Determine its Helmholtz free energy  $F$ .
5. Determine its entropy  $S$ .

**Problem 104 (Equations of state)**

An unknown substance is experimentally found to satisfy the following equations of state:

$$T(u, v) = au^{2/3}v^{-1/2} \quad \text{and} \quad P(u, v) = buv^{-1}$$

where  $a$  and  $b$  are some constants,  $T$  and  $P$  are the substance's temperature and pressure as functions of its internal energy per particle,  $u$ , and volume per particle,  $v$ , respectively.

1. Find the condition(s) under which the above two equations of state are consistent with each other, and then determine the entropy per particle of the substance,  $s(u, v)$ , to within an additive constant
2. Fix the constant in your answer to the previous part by invoking some law in thermodynamics.

**Problem 105 (Quasistatic process)**

A non-ideal gas has a fundamental relation given by

$$U(S, V, N) = \frac{1}{2A} S^2 V^{-1/2} N^{-1/2}$$

where  $U$  is the total internal energy,  $S$  is the total entropy,  $V$  is the volume,  $N$  is the number of molecules, and  $A$  is a constant.

1. Determine the following equations of state

$$U(T, V, N) \quad \text{and} \quad P(T, V, N).$$

- 
2. Consider a rigid chamber of volume  $V_0$  which is subdivided by an impermeable membrane into volumes  $V_0/3$  and  $2V_0/3$ . The chamber is isolated from the rest of the universe so that no heat or work can be transferred between them. (You may assume that the walls of the chamber have negligible heat capacity) A number  $N$  of molecules of the gas of the previous part is placed in the smaller section (volume  $V_0/3$ ), and the larger section is evacuated. Initially, the gas has internal energy  $U_0$ , temperature  $T_0$  and entropy  $S_0$ . Solve the following two parts of this problem under these conditions.
    - a If the membrane separating the two sections is broken, so that the gas can freely expand to fill the entire chamber, what are the final values of the internal energy  $U_f$ , temperature  $T_f$ , and entropy  $S_f$  of the gas after equilibrium has been reached? Express your answer in terms of  $U_0$ ,  $T_0$ , and  $S_0$ .
    - b If the gas is then slowly compressed isothermally back to its original volume, how much work is done by the piston compressing the gas? Express your answer in terms of  $U_0$ ,  $T_0$ , and  $S_0$ .

### Problem 106 (Ideal gas)

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1. A gas of  $N$  inert atoms (such as Ne or Ar) is contained in a volume  $V$  which may be taken as a cube of side  $L = V^{1/3}$  with periodic boundary conditions. The gas is in thermal equilibrium with the walls of the container which are maintained at (absolute) temperature  $T$ . Calculate the number of atoms in this gas with atomic kinetic energy larger than  $rk_B T$ , where  $r$  is some positive rational number (such as 2.0). Your answer may contain a dimensionless, unevaluated integral. You may neglect any interaction between the gas atoms, and treat the gas with Boltzmann statistics.
2. Will your answer change if the gas is made of  $N$  diatomic molecules (such as  $N_2$  or CO), if by kinetic energy we now mean the center-of-mass kinetic energy of a molecule? Briefly justify your answer.

### Problem 107 Quantum oscillator

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A quantum particle of charge  $q$  is in the potential  $V(x) = m\frac{\omega^2 x^2}{2}$  in 1D at temperature  $T$ .

1. Find the heat capacity of this system.
2. Find the electric dipole susceptibility of the system. ( $d = -(\partial F/\partial \mathcal{E})_{V,N,T}$ ,  $\chi = (\partial d/\partial \mathcal{E})_{V,N,T}$  where  $\mathcal{E}$  is the electric field.)
3. For the oscillator state  $\psi_n$  in the presence of electric field  $\mathcal{E}$  calculate  $x_n = \langle \psi_n | \hat{x} | \psi_n \rangle$ , and then average displacement  $\bar{x} = \sum_n x_n \omega_n$ .

## 2 Graduate level

### Problem 108 (Thermodynamic relations)

1. Show that

$$\left(\frac{\partial S}{\partial P}\right)_T = -\alpha V,$$

where  $\alpha$  is the coefficient of thermal expansion.

2. Show that for an isothermal compression

$$dE = (-T\alpha V + PV\beta_T) dP,$$

where  $\beta_T$  is the isothermal compressibility. To get the full credit for this problem you must start with  $dE = TdS - PdV$ .

### Problem 109

1. What is the average energy of a system at temperature  $T$  with two quantum states, with an energy difference  $\epsilon$  separating the levels?
2. In a highly disordered solid it is believed that a large number of two-level “tunneling” systems are present with a distribution of energy differences. If the number of these two level systems per unit volume of the solid with energy separations between  $\epsilon$  and  $\epsilon + d\epsilon$ ,  $D(\epsilon)$ , is a constant, show that their contribution to the heat capacity of the solid will be linear in temperature.

### Problem 110 1D classical particle in a potential

A classical one dimensional particle, confined to the region  $y \geq y_0$  is in a potential

$$V(y) = V_0 \log(y/y_0)$$

The statistical distribution is given by  $\varrho(p, q) = Ae^{-E(p, q)/T}$ , where  $A$  is a normalization parameter,  $T$  is a parameter which is called temperature, and  $E(p, q)$  is the particle’s energy.

1. Find the normalization constant  $A$ . Determine the critical temperature  $T_c$  above which the particle escapes to infinity (You need to figure out what it means.)
2. Write down the normalized positional distribution function  $f(y)$  (i.e. the probability per unit distance to find the particle between  $y$  and  $y + dy$ ) for this particle for  $T < T_c$ .
3. Find the average distance  $\langle y \rangle$  for the particle. What happens if  $0 < T_c/2 - T \ll T_c/2$ ?

### Problem 111

A thermodynamic system consists of  $N$  spatially separated noninteracting subsystems. Each subsystem has non-degenerate energy levels  $0, \epsilon, 2\epsilon$ , and  $3\epsilon$ . The system is in thermal equilibrium with a heat reservoir of absolute temperature  $T = \epsilon/k_B$ . Calculate the partition function, the mean energy, and the entropy of the thermodynamic system.

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**Problem 112**

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At  $T = 0$ , all the  $N$  atoms in a crystal occupy a lattice site of a simple cubic lattice with no vacancies. At higher temperature, it is possible for an atom to move from a lattice site to an interstitial site in the center of a cube (the interstitial atom does not have to end up close to vacancy). An atom needs energy  $\epsilon$  to make this transition.

1. Compute the number of different ways of making  $n$  vacancies (and correspondingly fill  $n$  interstitial sites) in the lattice.
2. Calculate the entropy of a state with energy  $E = n\epsilon$ .
3. Calculate the average  $\langle n \rangle$  in equilibrium at temperature  $T$ .
4. Calculate the free energy of the lattice at temperature  $T$ .

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**Problem 113 (Thermodynamics of magnetic materials)**

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A paramagnetic salt contains a total of  $10^{24}$  non-interacting magnetic ions, each with a magnetic moment of 1 Bohr magneton ( $9.273 \times 10^{24} \text{ Am}^2$ ) which can be aligned either parallel or anti-parallel to a magnetic field. A magnetic field of magnetic induction 1T is applied at a temperature 3K.

1. Calculate the partition function.
2. Compute the magnetic energy.
3. Compute the heat capacity.

[**Hint:** You will be given more credit for this problem if you can also give numerical values for the last two parts.]

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**Problem 114 (Fermi gas)**

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1. Find the mean speed of the fermions in an ideal  $D$ -dimensional Fermi gas at  $T = 0$  (the dispersion is  $\epsilon_p = p^2/2m$ ) in terms of  $v_F$  - Fermi velocity (velocity at  $\epsilon_F$ ).
2. Find the average kinetic energy of a fermion in terms of  $v_F$ .

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**Problem 115 (Quantum mechanics)**

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The single particles energy levels for a particular Hamiltonian are  $\epsilon_n = n\epsilon$ . where  $n = 1, 2, 3, \dots$ . For a system of three non-interacting identical particles in the same spin state, find the energy and the degeneracy of the ground state and the first four excited states if the particles are:

1. Bosons.
2. Fermions.
3. What is the energy and degeneracy of the ground state and the first four excited states if the system consists of spin 1/2 particles which are not constrained to be in the same spin state?

**Problem 116 (Landau theory of phase transitions)**

Remembering that the free energy  $F$  will be minimized in a given phase, and that the “order parameter” is defined to be zero above a phase transition, consider a system whose free energy  $F$  depends on an order parameter  $\phi$  according to

$$F(\phi, T) = F_0 + a(T - T_c)\phi^2 + b\phi^4$$

where  $F_0$ ,  $a$ , and  $b$  are all positive constants. Show that there is a phase transition at a temperature  $T_c$  and deduce the temperature dependence of the order parameter. Calculate the jump in the heat capacity at  $T = T_c$ .

[Hint:  $C = -T(\partial^2 F / \partial T^2)$ .]

**Problem 117 (Thermodynamics for a two level system)**

A system consists of  $N$  weakly interacting particles each of which can be in either of the two states with respective energies  $\epsilon_1$  and  $\epsilon_2$ , with  $\epsilon_1 < \epsilon_2$ .

1. Make a qualitative plot of the mean energy  $\bar{\epsilon}$  of the system as a function of the temperature  $T$ . What is  $\bar{\epsilon}$  in the limit of very low and very high temperatures? Roughly at what temperature does  $\bar{\epsilon}$  change from its low to its high temperature value?
2. Using the result of the previous part make qualitative plot of the heat capacity  $C_V$  as a function of the temperature  $T$ .
3. Calculate explicitly an expression for the mean energy  $\bar{\epsilon}(T)$  and heat capacity  $C_V(T)$  for this system. Verify that your expression exhibit the qualitative features discussed in the previous parts.

**Problem 118 (Bose Einstein statistics)**

1. For a photon gas, show that the average number of photons in a particular state,  $s$ , is given by

$$n_s = \frac{1}{e^{\beta\epsilon_s} - 1},$$

where  $\epsilon_s$  is the energy of the state  $s$ , and  $\beta = 1/k_B T$ .

2. Calculate the density of modes i.e. the number of modes per unit volume between  $\omega$  and  $\omega + d$  for a three dimensional photon gas.
3. Show that the average energy density  $\bar{u}$  of the gas can be written as

$$\bar{u}(\omega, T)d\omega = \frac{h\omega^3 d\omega}{\pi^2 c^3 (e^{\beta h\omega} - 1)}$$

4. Show that  $h\omega_{\max}/k_B T \approx 3$ , where  $\omega$  represents the peak in the energy density functional.
5. Show that the energy density functional is proportional to  $T^4$ .  
[Hint: Change the energy  $h\omega$  to a dimensionless variable.]

**Problem 119 (Quantum thermodynamics)**

Suppose we have some type of wavelike excitation in a solid which is characterized by a free quasiparticle of spin 3. The total number of quasiparticles in the system is not conserved. Furthermore, the excitation (quasiparticle) obeys the dispersion relation  $\omega = Ak^3$ , where  $\omega$  is the angular frequency of the excitation,  $k$  is its wave number, and  $A$  is a constant of proportionality. If the solid has a volume  $V$  and is macroscopic in size, then determine the temperature dependence of both the internal energy and heat capacity in the limit of very low temperatures.

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### Problem 120 (Quantum statistics)

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There are three quantum states of energies  $0$ ,  $\epsilon$ , and  $2\epsilon$ . Consider a system of two indistinguishable non-interacting particles which can occupy these states. The system is coupled with the heat bath at temperature  $T$ .

1. Calculate the free energy of the system in case the particles are Bosons.
2. Calculate the free energy of the system in case the particles are Fermions.
3. What is the ratio of occupation probability of the highest energy state of the system to the lowest energy state in each of these cases?

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### Problem 121

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A sample of water is placed in an external magnetic field  $B$ . Each proton has a spin  $1/2$  and a magnetic moment  $\mu$ . An applied radio-frequency field can induce transitions between the magnetic (Zeeman) energy levels, (How many possible energy levels per proton are there?), if the frequency  $\nu$  satisfies the Larmor condition  $h\nu = 2\mu B$ . The power absorbed from the radiation field is then proportional to the difference in the number of protons in the energy levels. Assume that the protons in the water are in thermal equilibrium at temperature  $T$  such that  $\mu B \ll k_B T$ .

1. Give an expression for the partition function.
2. How does the absorbed power depend on the temperature of the water?

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### Problem 122 (Density of states)

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If  $D(\epsilon)$  is a density of states function, find an expression for the heat capacity of a fermion gas at  $k_B T \ll \epsilon_F^0$ , even if  $D(\epsilon)$  is a complicated function of energy  $\epsilon$ .

[**Hint:** The expression for the heat capacity should contain  $D(\epsilon)$ ,  $T$ , and some constants.  $\epsilon_F^0$  is the chemical potential at absolute zero. You may need the integral

$$\int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2} dx = \frac{\pi^2}{3}.$$

]

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### Problem 123 1D oscillator, quantum vs classical

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In one-dimension, a mass  $m$  is attached to a spring of spring constant  $k$ . The system is in thermal equilibrium at a temperature  $T$ .

1. Assuming the classical statistics hold, what is the rms displacement of the mass from equilibrium, if  $T = 70^\circ\text{F}$ ,  $m = 2\text{g}$ , and  $k = 50\text{g/s}^2$ . Take  $k_B = 1.4 \times 10^{-16}\text{cgs}$  and  $\hbar \approx 10^{-27}\text{cgs}$ .
2. Treating this system using quantum statistics, where the energy of the system is  $E = \hbar\omega(n + 1/2)$  for  $n = 0, 1, \dots$ , and there is only one state at each energy, calculate the partition function of this system. ( $\omega$  is the oscillation frequency of the mass on the spring.)
3. What is the average energy  $\bar{E}$  of the system? Does this come close to the classical value for the system in the first part?
4. From the previous part, find the average occupation number  $\bar{n}$ . Must  $\bar{n}$  be large or small for  $\bar{E}$  to be close to its classical value?
5. Give an approximate criterion for the validity of the classical result.



### Problem 124 3D quantum oscillator

A 3D harmonic oscillator has mass  $m$  and the same spring constant  $k$  for all three directions. Thus, its quantum-mechanical energy levels are given by

$$E = \hbar\omega (n_1 + n_2 + n_3 + 3/2)$$

Neglect the zero point energy in what follows.

1. What are the energy  $E_0$  and degeneracy  $g_0$  of the ground state? Of the first excited state? Of the second excited state?
2. What is the partition function for this system if only the lowest two (ground and the first excited) energy levels are important? When is this approximation valid?
3. What is the free energy in this case?
4. What is the entropy in this case?
5. What is the rms fluctuation  $\delta E \equiv \left( \overline{E^2} - (\overline{E})^2 \right)^{1/2}$  in the energy in this case?

### Problem 125 (Two level system)

Consider a large number  $N$  of identical non-interacting particles, each of which can be in only one of two states, with energies  $\epsilon_0$  and  $\epsilon_1$ . Denote by  $n_0$  and  $n_1$  the occupation numbers of each of these states.

1. Find the total energy  $E$  as a function of  $n_0$ .
2. Find the number of states  $N$  available to the system, as a function of  $n_0$ .
3. Find  $S$ , the entropy, as a function of  $E$ .
4. Find the temperature  $T$  as a function of  $E$ .
5. Using  $E_0 = N\epsilon_0$  and  $\Delta\epsilon = (\epsilon_1 - \epsilon_0)$ , show that

$$E = E_0 + \frac{N\Delta\epsilon}{1 + \exp[\Delta\epsilon/k_B T]}$$

[Hint:  $\log n! \approx n \log n - n$ , for large  $n$ .]

### Problem 126 2D Fermi gas

1. Find the Fermi energy at  $T = 0$ ,  $\epsilon_F$ , of a gas of  $N$  non-interacting spin one-half particles constrained to move in two dimensions.
2. Recall that the surface tension,  $\sigma$ , in two dimensions is analogous to pressure in three dimensions so that the surface tension contribution from a particle in a state  $n$  is given by  $-\partial\epsilon_n/\partial A$ . Show that the surface tension at  $T = 0$  is given by  $N\epsilon_F/2A$ , where  $A$  is the area that the particles occupy.

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**Problem 127 (Ideal gas; van der Waals gas)**

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1. Show that for an ideal gas, for a quasistatic adiabatic process

$$\frac{dP}{dV} = -\gamma \frac{P}{V}$$

where  $\gamma = C_P/C_V$ .

2. Write down the expression for the work done by one mole of a monoatomic ideal gas during an adiabatic expansion from a state  $(P_1, V_1)$  to a state with volume  $V_2$ .
3. The molar energy of a monoatomic gas which obeys van der Waals' equation of state is given by

$$E = \frac{3}{2}RT - \frac{a}{V},$$

where  $V$  is the molar volume at a temperature  $T$  and  $a$  is a constant of the gas. If initially, one mole of the gas is at the temperature  $T_1$  and occupies volume  $V_1$ , and the gas is allowed to expand irreversibly into a vacuum in an isolated container, so that it occupies a total volume  $V_2$ , what is the final temperature  $T_2$  of the gas?

4. Calculate the change of the temperature in this process for the ideal gas. Give the reason for your answer explaining concisely the origin of the differences (**In one short(!!!!) sentence.**).

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**Problem 128 (Thermodynamic equilibrium)**

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For a vapor in equilibrium with its solid phase, find the relation between the pressure  $P$  and the temperature  $T$ , if the molar latent heat  $q$  is constant. The vapor is close to the ideal gas, and the molar volume of the gas is much larger than that of solid.

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**Problem 129 Two chambers**

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A thermally isolated container is divided by a partition into two compartments, the right hand compartment having a volume  $b$  times larger than the left one. The left compartment contains  $\nu$  moles of an ideal gas at temperature  $T$ , and pressure  $P$ . The right compartment also contains  $\nu$  moles of an ideal gas at temperature  $T$ . The partition is now removed. Calculate:

1. The final pressure.
2. The total change in the entropy if the gases are different.
3. The total change in the entropy if the gases are the same.
4. What is the total change in the entropy if the gases are the same and  $b = 1$ ? Can you explain the result?

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**Problem 130 (Thermodynamic relations)**

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$N$  classical particles are constrained to move on a frictionless flat surface of area  $A$ .

1. What is the partition function for the system at the temperature  $T$ , assuming that the particles are distinguishable?
2. Same as above, if the particles are indistinguishable.

3. For indistinguishable particles, compute the free energy  $F$ .
4. For indistinguishable particles, compute the entropy  $S$ .
5. Verify that, if  $N \rightarrow 2N$  and  $A \rightarrow 2A$ , then  $S \rightarrow 2S$ . What role indistinguishability have to play in this result?
6. Let  $\sigma$  represent the two-dimensional pressure, or surface tension, of this system. Find  $\sigma$  as a function of  $N$ ,  $T$ , and  $A$ .

### Problem 131 (Chemical potential; Bose Einstein statistics)

Consider a system of  $N \gg 1$  non-interacting bosons of spin zero, with quantum states at the single particle energies 0 and  $\epsilon$ . The thermal average population of the lowest state is twice the population of the state with energy  $\epsilon$ . Find approximate values of the chemical potential  $\mu$  and the temperature  $T$ .

### Problem 132 Vacancy formation

A model for a vacancy formation in an otherwise perfect crystal is as follows. An energy  $E_s$  is required to produce a vacancy by taking an atom from the interior and putting it on the surface. Let the number of lattice sites in the bulk  $N$  greatly exceed the number of vacancies  $n$ , and let  $n \gg 1$ .

1. In how many ways can one take  $n$  atoms from the interior? Treat the atoms as indistinguishable.
2. What is the entropy  $S$  associated with this?
3. What is the energy of the system, assuming that  $E = 0$  in the absence of vacancies?
4. For a given temperature  $T$ , what is the thermal average value of  $n$ ?

### Problem 133 (Cyclic process)

Consider a cyclic engine operating with one mole of an ideal monoatomic gas in between two baths with temperatures  $T_a$  and  $2T_a$  in the cycle  $a \rightarrow b \rightarrow c \rightarrow d \rightarrow a$ .  $V_a$  and  $T_a$  are the volume and the temperature of the gas in point  $a$ .

$a \rightarrow b$  is isobaric increase of temperature from  $T_a$  to  $2T_a$ .

$b \rightarrow c$  isothermal expansion to the volume  $3V_a$ .

$c \rightarrow d$  decrease of temperature back to  $T_a$  at constant volume.  $d \rightarrow a$  isothermal compression back to the volume  $V_a$ .

All processes are reversible.

1. Calculate the efficiency of this engine and compare it to the maximum possible efficiency for an engine operating between  $T_a$  and  $2T_a$ .
2. What is the net entropy change of the gas in one cycle?
3. What is the net change of the energy of the gas in one cycle?
4. What is the net change of the entropy of the hot thermal bath during one cycle, if all processes are reversible?
5. What is the net change of the entropy of the cold thermal bath during one cycle, if all processes are reversible?

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**Problem 134 (Partition function)**

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Write down the partition function for an ideal gas of  $N$  monoatomic molecules in a volume  $V$  in a classical limit where you have treated the particles as distinguishable. What is the partition function in the classical limit if the particles are indistinguishable? Use both partition functions to calculate the entropy of the ideal gas in each case. Why is the result for the distinguishable particles physically unacceptable?

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**Problem 135 (Two level system)**

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1. Consider a particle which can take one of only two energy levels ( $E = 0$  or  $E = \epsilon$ ). Find and sketch as a function of  $T$  the average energy  $E(N, T)$  and the heat capacity  $C_V(N, T)$  for a system of  $N$  particles. The particles are distinguishable.
2. Suppose that the value of the excited state energy  $\epsilon$  varies for different particles in a system of  $N$  particles. Furthermore, assume that the number of particles with a particular value of the excited state energy between  $\epsilon$  and  $\epsilon + d\epsilon$  is  $n(\epsilon)d\epsilon$  and suppose that  $n(\epsilon)$  is a constant for all energies between 0 and  $\epsilon_0$ , and that there is no states with  $\epsilon > \epsilon_0$ , i.e.

$$n(\epsilon) = \begin{cases} n_0, & \text{for } 0 < \epsilon \leq \epsilon_0 \\ 0, & \text{for } \epsilon > \epsilon_0 \end{cases}$$

and  $N = \int_0^{\epsilon_0} n(\epsilon)d\epsilon = n_0\epsilon_0$ . Find the temperature dependence of the specific heat of these  $N$  particles at low temperature,  $T \ll \epsilon_0/k_B$ .

---

**Problem 136 (Observables)**

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Consider a system of  $N$  noninteracting particles in a volume  $V$  at an absolute temperature  $T$ . The single particle energy states are described by  $\epsilon_i = \hbar^2 k_i^2 / 2m$ . For convenience, assume that the  $k_i$  are determined by periodic boundary conditions.

1. Show that the mean pressure  $\bar{P}$  of the system is given quite generally in terms of the average kinetic energy  $\bar{E}$  by

$$\bar{P} = \frac{2\bar{E}}{3V}$$

independent of whether the particles obey classical, Fermi-Dirac, or Bose-Einstein statistics.

2. Show that the dispersion in pressure of this system,  $\overline{(\Delta P)^2} = \overline{(P - \bar{P})^2}$ , is given by

$$\overline{(\Delta P)^2} = \frac{2k_B T^2}{3V} \left( \frac{\partial \bar{P}}{\partial T} \right)_{N,V}$$

---

**Problem 137 Spin-1/2 particles in a magnetic field**

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Consider  $N$  identical and independent particles of spin 1/2 in a magnetic field so that the energy of each particle is either  $\epsilon$  or  $-\epsilon$  depending upon the orientation of the spin: down or up respectively. The probability of the energy  $-\epsilon$  is  $p$  and of  $+\epsilon$  is  $q = 1 - p$ .

1. Find the probability that  $N_1$  spins are up and  $N_2$  are down, with  $N_1 + N_2 = N$ .
2. From this probability find the average or expected value of the energy in terms of  $p$ ,  $\epsilon$ , and  $N$ .

3. By considering that  $N_1$  and  $N_2$  are continuous rather than discrete variables, find the most likely (i.e., maximal probability) for the values  $N_1$  and  $N_2$  using the approximation that  $\log(x!) \approx x \log(x) - x$ .
4. Write down a partition function for this system at a temperature  $T$ .
5. Find the free energy, the entropy, and the total energy from this partition function. For what value of  $p$  will your result in the second part agree with your result for the total energy in this part?

### Problem 138 (Classical degenerate system)

Consider a classical system of  $N$  weakly interacting particles. Each isolated particle can be in  $n$  states. Assume the ground state degeneracy of the system is  $a$ , where  $1 \leq a < n$ . The excited energy levels are on the average evenly distributed around a characteristic energy  $E_1$ . There are no phase changes in the phase diagram for the system.

1. Sketch entropy per particle ( $N \rightarrow \infty$ ) as function of temperature in the entire temperature range. Write and denote on the graph the values of entropies and of characteristic temperature you can determine from the given information.
2. Sketch the specific heat  $C_V$  as function of temperature using  $C_V/T$  and  $T$  as coordinate axes. What is the total area under the curve?
3. Answer the first part now assuming that the levels are not all evenly distributed, but rather  $m$  out of  $n$  states have characteristic energy  $E_2$  at least an order of magnitude larger than the characteristic energy  $E_1$  of the remaining states.

### Problem 139 Rotating fluid

An incompressible fluid of density  $\rho_f$  is confined to a very long (infinite) cylinder of cross section  $A$  with which it rotates at a constant angular velocity  $\omega$  around a perpendicular axis through the middle-point of the cylinder, Fig. ???. Small number of microscopic spheres each of volume  $v$  and density  $\rho_s < \rho_f$  are immersed in the rotating fluid at temperature  $T$ . Neglect any interaction between the spheres, find the average distance of a sphere from the rotation axis.

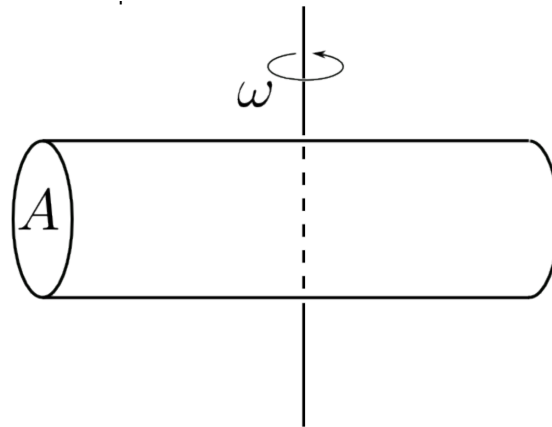


Figure 0.1: rotating fluid

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**Problem 140 (Thermodynamic relations)**

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A certain solid material has an isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

Prove that adiabatic and pressure changes are related by

$$\frac{dV}{V} = -\kappa_T \frac{C_V}{C_P} dP$$

where  $C_V$  and  $C_P$  are the specific heats of the material at constant volume and pressure respectively.

---

**Problem 141 (van der Waals gas)**

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Consider a monoatomic van der Waals gas whose equation of state is

$$P = -\frac{a}{V^2} + \frac{RT}{V-b}$$

If this gas undergoes free expansion,

1. What is the change in temperature in terms of the initial volume  $V_1$  and final volume  $V_2$ ?
2. Determine the change in entropy.

[Hint:  $C_V$  for a monoatomic van der Waals gas is a temperature and volume independent constant.]

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**Problem 142 Electrons in a metal**

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Let  $\epsilon_{\vec{p}} = \rho(|p_x| + |p_y| + |p_z|)$  be the energy-momentum relation of conducting electrons in a certain (fictitious) metal, where  $\rho$  is a constant with the dimensions of velocity, and  $|x|$  denotes the absolute value of  $x$ .

1. Draw a picture of a typical constant-energy surface  $\epsilon_{\vec{p}} = \epsilon$ , for the above dispersion  $\epsilon_{\vec{p}}$ .
2. Express the Fermi energy  $\epsilon_F$  as a function of the electron density  $n$  for this metal. (Note, that electrons have spin 1/2.)
3. Calculate the electronic density of states (per unit volume) as a function of  $\epsilon$  for this metal. Denote it as  $D(\epsilon)$ .
4. Calculate the total energy of  $N$  electrons at  $T = 0$  in this metal. Express  $E_0/N$  in terms of  $\epsilon_F$ .
5. Now let the temperature  $T$  be finite. Express  $N$  and the total energy  $E$  as functions of  $T$  and the chemical potential  $\mu$ . The expressions can involve integrals which you do not have to evaluate.

---

**Problem 143 (Mean field theory)**

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Show that the van der Waals equation of state can be derived from a mean field theory: Assume that the potential felt by each particle in a gas is

$$u(r) = \begin{cases} \infty, & \text{for } r < r_0 \\ -\bar{u}, & \text{otherwise} \end{cases}$$

where

$$\bar{u} = cN/V$$

Here  $N/V$  is the number of particles per unit volume, and  $c$  is a constant. (First evaluate the classical partition function  $Z$ , and then use it to find pressure  $P$ .) Give physical interpretation of your finite answer (the van der Waals equation), and show that it reduces to the correct result when  $u(r) = 0$ .

**Problem 144 (Boltzmann gas)**

A system of ideal Boltzmann gas containing  $N$  monoatomic molecules (of mass  $m$  each) is trapped in a three-dimensional harmonic potential well  $V(x, y, z) = \frac{1}{2}K(x^2 + y^2 + z^2)$ , so it will form a spherical cloud whose room-mean-square radius  $\bar{r} \equiv (x^2 + y^2 + z^2)^{1/2}$  will be the function of temperature. Calculate:

1. The (quantum) canonical partition function, (which no longer has volume  $V$  as an independent variable due to the trapping potential)
2. The free energy  $F(N, T)$ .
3. The total entropy of the cloud  $S(N, T)$ .
4. Take the high-temperature approximation of  $S(N, T)$  to the leading order in some small parameter, and use it to obtain the specific heat  $C(N, T)$  in this limit to the same order. (Note: the specific heat is not of constant volume, nor of constant pressure, but of constant  $K$ , the force constant, and, of course, constant  $N$ .)
5. Interpret your result from the previous part in light of the equipartition theorem.
6. Given that  $\langle n|x^2|y\rangle = (n + 1/2)\hbar\omega_0/K$  for a quantum mechanical harmonic oscillator of mass  $m$  and force constant  $K$ , calculate  $\bar{r}_{\text{rms}}$ , and hence the “mean” volume  $\bar{V} \equiv \frac{4\pi}{3}\bar{r}_{\text{rms}}^3$ , of the above cloud as a function of  $N$  and  $T$ . What is the smallest  $\bar{V}$  at any temperature, and what is the behavior of  $\bar{V}$  with respect to  $T$  in the high-temperature limit?

**Problem 145 Heat capacity at low temperatures**

Show that in two dimensions, the heat capacity  $C_V$  at low temperatures is the same for fermions and bosons. **[Hint:**

$$\int_0^\infty \frac{x^2 e^x dx}{(e^x - 1)^2} = \int_{-\infty}^\infty \frac{x^2 e^x dx}{(e^x + 1)^2} = \frac{\pi^2}{3}$$

]

**Problem 146 (Two level system)**

A system has only two energy levels. The lower energy level with energy  $E = -E_0$  is non-degenerate, and the higher energy level with energy  $+2E_0$  is three-fold degenerate.

1. Assuming that the system is in thermodynamic equilibrium with its surroundings which are maintained at an absolute temperature  $T$ , what are the probabilities that the system is found in each of the two energy levels?
2. If the volume of this system is  $V_0$  when it is in the lower energy state, but it increases to  $1.2V_0$  when it is in the higher energy state, calculate the mean volume  $\langle V \rangle$  of this system as a function of temperature, and its thermal expansion coefficient  $\alpha$  as a function of temperature.
3. What is expected limiting value of  $\alpha$  as  $T \rightarrow \infty$ ? What about  $\langle V \rangle$  itself? Use these limiting behaviors to check your results of the previous part.

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**Problem 147 (Open system)**

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A system contains two different types of excitations whose numbers are not conserved. One type consists of bosons such that the number of excitation modes with energy between  $\epsilon$  and  $\epsilon + d\epsilon$  is

$$\frac{V}{2\pi^2} \frac{\epsilon^2}{c^3} d\epsilon$$

The other consists of fermions such that the number of excitation modes with energy between  $\epsilon$  and  $\epsilon + d\epsilon$  is

$$\begin{cases} 0 & \text{for } \epsilon < \epsilon_0 \\ \frac{2V}{3\pi^2 b} d\epsilon & \text{for } \epsilon > \epsilon_0 \end{cases}$$

$V$  is the volume of the system and  $b$  and  $c$  are constants.

1. Calculate the average energy of the system as a function of temperature  $T$ .
2. Calculate the specific heat per unit volume of the system as a function of temperature.

**[Hint:** One of the integrals can only be done after a series expansion, using

$$\frac{1}{e^x + 1} = \sum_{n=1}^{\infty} (-1)^{n+1} e^{-nx}, \quad \int_{x_0}^{\infty} x e^{-ax} dx = \frac{1}{a} x_0 e^{-ax_0} + \frac{1}{a^2} e^{-ax_0}$$

Also you might need some of the following definite integrals:

$$\int_0^{\infty} \frac{x dx}{e^x - 1} = \frac{\pi^2}{6}, \quad \int_0^{\infty} \frac{x^2 dx}{e^x - 1} = 2\zeta(3), \quad \int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}, \quad \int_0^{\infty} \frac{x^4 dx}{e^x - 1} = 24\zeta(5)$$

where  $\zeta(x)$  is the Riemann zeta function.]

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**Problem 148 (Nuclear magnetic moments)**

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Consider a system of  $N$  non-interacting nuclei with a spin quantum number  $I$ . Find an expression for the magnetization  $M$  and the entropy  $S$  of these nuclei at a temperature  $T$  in a magnetic field  $B$ . Express your answer in terms of  $g$ , the Landé g-factor for this nucleus, and  $\mu_B$ , the Bohr magneton. Indicate the high temperature and low temperature limits for  $M$  and  $S$ . How could the nuclear magnetic moments be used to cool the material?

**[Hint:** Useful relations:

$$\begin{aligned} 1 + x + x^2 + \cdots + x^n &= (1 - x^{n+1}) / (1 - x) \\ \sinh x &\equiv (e^x - e^{-x}) / 2 \\ \frac{d \sinh x}{dx} &= \cosh x \equiv (e^x + e^{-x}) / 2 \end{aligned}$$

]

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**Problem 149 (Fermi gas)**

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Consider  $N$  spin-1/2 (fermionic) atoms of a monoatomic gas that might be physically adsorbed on a homogeneous surface of area  $A$ . Assume that the atoms are noninteracting and that the energy of a single such atom would be described quantum mechanically by

$$\epsilon = (p_x^2 + p_y^2) / 2m - \epsilon_0$$

where  $\epsilon_0$  is the binding energy of the atom to the surface and is same for all of the atoms.



1. Calculate the  $T = 0$  value of the chemical potential  $\mu$  for these atoms as a function of the area density  $N/A$ , binding energy  $\epsilon_0$ , and mass  $m$ .
2. At temperatures very close to  $T = 0$  (i.e., so that you can ignore any temperature dependence of the quantities you might calculate for the adsorbed fermions,) find the areal coverage  $N/A$  of adsorbed atoms as a function of the density  $\rho \equiv N'/V'$  and temperature  $T$  of a dilute (three-dimensional) gas of the same atoms that is in thermal equilibrium with the adsorbed gas. Assume that the dilute gas can be treated classically at the given temperature with the partition function

$$Z = \frac{1}{N'!} \left( \frac{m}{2\pi\hbar^2\beta} \right)^{3N'/2} (2V')^{N'}$$

and  $\beta \equiv 1/k_B T$ .

### Problem 150 (Equations of state)

Consider an ideal classical gas of rigid dipolar molecules in an electric field  $E$ . The dipole moment of each molecule is  $\mu$ . Calculate the linear dielectric constant  $\epsilon$  of the gas as a function of temperature  $T$  and density  $\rho = N/V$ .

### Problem 151

In experiments on the absorption spectrum of gases at finite temperature, atoms are always moving either towards or away from the light source with distribution of velocities  $v_x$ . As a consequence the frequency of the photon seen by an electron in a Bohr atom is Doppler shifted to a value  $\nu_d$  according to the classical formula

$$\nu_d = \nu_0 (1 + v_x/c)$$

1. Write down the normalized Maxwell distribution for  $v_x$ .
2. Determine the distribution function  $g(\nu_d)$  for the fraction of gas atoms that will absorb light at frequency  $\nu_D$
3. Determine the fractional linewidth

$$\left( \frac{\Delta\nu}{\nu_0} \right)_{rms} \equiv \sqrt{\left\langle \frac{(\nu_d - \nu_0)^2}{\nu_0^2} \right\rangle}$$

4. Estimate the fractional linewidth for a gas of hydrogen ( $M \approx 938 MeV/c^2$ ,  $1 eV/k_B \approx 11600 K$ )

### Problem 152

A system obeys the van der Waals equation of state,

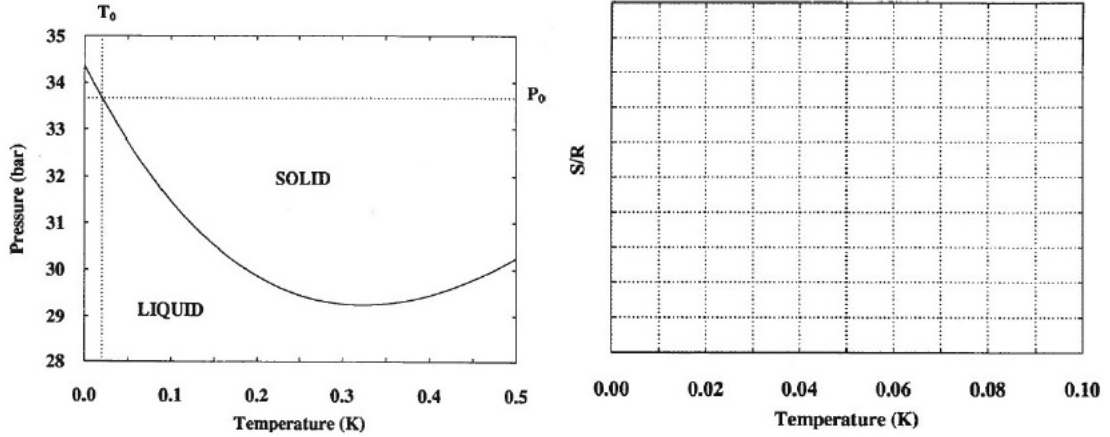
$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

where  $P$  is pressure,  $v$  is the molar volume,  $T$  is the absolute temperature, and  $R$ ,  $a$ , and  $b$  are all constants. The molar heat capacity at constant volume  $c_V$  is given as a constant independent of  $P$ ,  $T$ , and  $v$ .

1. One mole of this system is expanded isothermally at temperature  $T$  from an initial volume  $v_i$  to a final volume  $v_f$ . Find heat transfer to the system in this process.

2. One mole of this system is expanded from an initial volume  $v_i$  to a final volume  $v_f$  in a process that conserves the enthalpy  $H = U + PV$ . Such a process is often referred to a Joule-Thomson expansion, or a “throttling” process. Determine the change in the temperature  $T$  if the change in the volume is small  $v_f - v_i \ll v_f$

### Problem 153



The  $He^3$  melting curve (solid-liquid coexistence curve) is shown in the figure (left). The general shape of the melting curve is well understood in term of the physical properties of solid and liquid  $He^3$  and the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v}$$

where  $\Delta s$  and  $\Delta v$  are the molar entropy and molar volume differences between the two phases.

At low temperatures the molar volumes of the solid and liquid do not vary substantially along the coexistence curve such that below  $40mK$   $v_l - v_s$  is essentially a constant at  $1.3cm^3/mole$ .

The thermal properties of the solid can be modeled by a system of  $N$  independent 2-level systems with the energy gap of  $1mK$ , where  $N$  corresponds to the number of  $He^3$  atoms.

The thermal properties of the liquid at low temperatures are well described by a degenerate Fermi gas. In particular, the heat capacity of the liquid at temperatures below  $40mK$  is known to be linear in temperature, i.e.  $c_v \propto T$ .

You are given that the slope of the melting curve at  $P_0 = 33.66 \text{ bar}$  and  $T_0 = 20mK$  is

$$\frac{dP}{dT} = -38.43 \text{ bar/K}$$

1. Estimate the molar entropy of the solid  $s_s$  at  $P_0$  and  $T_0$ .
2. Using your result and the Clausius-Clapeyron equation, estimate the molar entropy  $s_l$  of the liquid at  $P_0$  and  $T_0$ .
3. Draw entropy as a function of the temperature along the  $P_0$  isobar from  $T = 0K$  to  $T = 0.1K$ . Important features in your graph should be labelled with the numerical values. Please use the graph provided.

### Problem 154

The energy-momentum dispersion relation for electrons in the extreme relativistic limit ( $\epsilon \gg m_0 c^2$ ) is well approximated by

$$\epsilon = pc$$

Assuming this relation is valid at all energies of interest, find:

1. The Fermi energy  $\epsilon_F$  at absolute zero in terms of the gas density,  $n = N/V$ .
2. The average energy per electron in the ground state of the gas at  $T = 0$  as a function of  $\epsilon_F$ .
3. Derive the equation of state for an electron gas in the extreme relativistic limit which is valid at **any temperature** when the dispersion relation given above applies.

### Problem 155

A gas consists of two molecular types,  $A$  and  $B$ , which are intermixed in a volume  $V$  at a constant temperature  $T$ . This is a non-ideal gas, but each molecular type acts as an independent indistinguishable particle system so that the energy for each type  $A$  molecule is given by

$$\epsilon_A = \frac{p^2}{2m_A} + \alpha n_A$$

and for each type  $B$  molecule as

$$\epsilon_B = \frac{p^2}{2m_B} + \alpha n_B + \epsilon_0$$

Here  $\alpha$  is a constant and  $\epsilon_0$  is a constant energy for a  $B$ -type molecule. The number densities of molecules  $A$  and  $B$  are  $n_A = NA/V$ , and  $n_B = NB/V$  respectively.

1. Determine the  $N$ -particle classical canonical partition function for this mixed gas. Since the partition function is to be determined classically, you can assume that there is only one state per volume of the phase space  $h^3$  for each of the two types of molecules.
2. Determine the Helmholtz free energy of this gas from the partition function.
3. Now, allow  $A$  and  $B$  type molecules to interconvert by simple reaction  $A \rightleftharpoons B$  (e.g.  $B$  might be excited state of  $A$  and vice versa). Also assume  $A$  and  $B$  have equal masses. Given that  $A$  and  $B$  are in equilibrium (at fixed  $V$ ,  $T$ , and total number of molecules,  $N = N_A + N_B$ ), determine the equilibrium ratio,  $R = N_A/N_B$ .

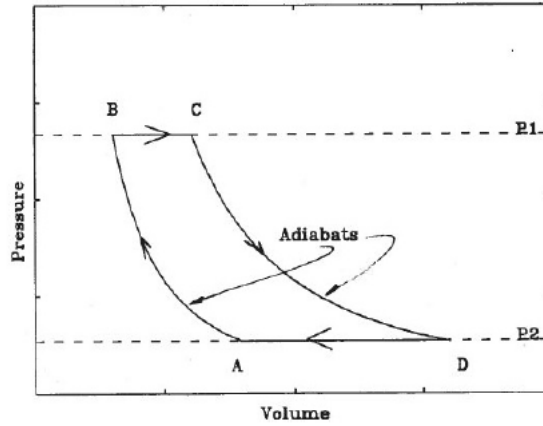
[**Hint:** Stirling's approximation,  $\ln N! = (N \ln N) - N$  . ]

### Problem 156

A particular ideal gas is characterized by the following equations of state:

$$PV = Nk_B T \quad \text{and} \quad U = cNk_B T,$$

where  $c$  is a constant. The gas is used as a medium in a heat engine/refrigerator whose cycle can be represented on a  $P - V$  diagram as shown in the figure.



1. Determine the change in the internal energy of the gas for one complete cycle ( $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$ ).
2. Determine the equation of the adiabats.
3. Determine the thermodynamic efficiency of the above heat engine. Express your answer in terms of  $c$ ,  $P_1$ , and  $P_2$ .

### Problem 157

Consider a monolayer  $He^3$  (spin=  $1/2$ ) film of a large area  $A$ , and assume that it behaves like a two-dimensional ideal gas.

1. Determine the Fermi energy ( $T = 0$ ) as a function of the coverage density  $\sigma = N/A$ .
2. Determine the chemical potential ( $T \neq 0$ ) as a function of the coverage density  $\sigma = N/A$ .
3. Determine how the heat capacity scales with temperature as  $T \rightarrow 0$  using the fact that the derivative of the Fermi function is sharply peaked around  $\epsilon_F$  in this limit.

### Problem 158

Consider a non interacting gas of  $He^4$  (spin= 0) confined to a film (i.e., confined in  $\hat{z}$  direction, but infinite in the  $x$  and  $y$  directions). Because of the confinement, the  $p_z$  component of the momentum is quantized into discrete levels,  $n = 0, 1, \dots$  so that the energy spectrum is

$$\epsilon_n(\mathbf{p}) = \frac{\mathbf{p}^2}{2m} + \epsilon_n$$

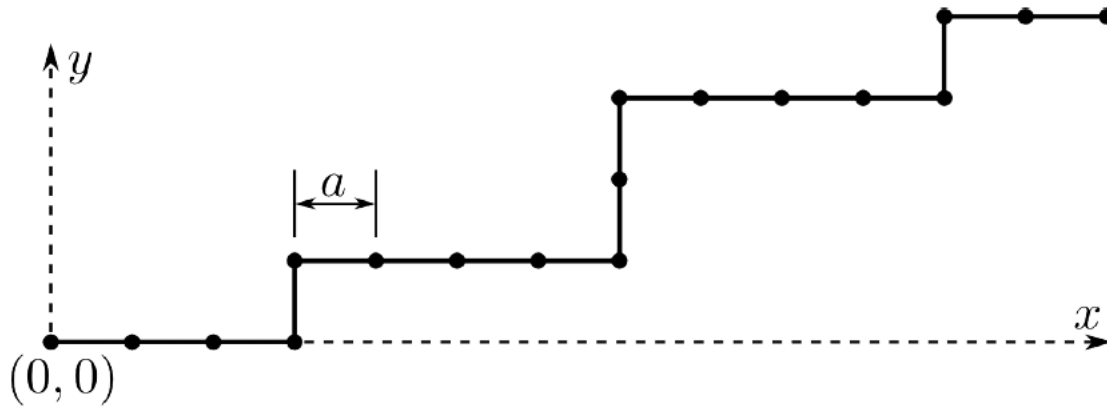
where  $\mathbf{p}$  is the two-dimensional ( $p_x, p_y$ ) momentum, and  $0 = \epsilon_0 < \epsilon_1 < \dots < \epsilon_n < \dots$ .

1. Write down the density of states for the system.
2. Write down the expression which determines the density of  $He^4$  atoms  $n$  as a function of a chemical potential  $\mu$  and temperature  $T$ . Evaluate integrals explicitly.
3. As  $T \rightarrow 0$ , i.e.  $T \ll \epsilon_1$  find the limiting value of  $\mu$  and how the specific heat depends on  $T$  in this limit.
4. Determine  $\mu(N, V, T)$  in the limit  $|\mu| \gg T$  (classical limit) assuming  $\epsilon_n = \epsilon n$ .

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**Problem 159**


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A two dimensional fictitious “polymer” is constructed as follows: It consists of  $N$  identical monomers of length  $a$  each, joined into a chain. (See figure). Starting from the left end of the “polymer”, which corresponds to the coordinates  $x = 0, y = 0$ , each new monomer added prefers to extend the “polymer” to the right (i.e., to the  $+x$  direction) with energy  $\epsilon = 0$ , or upward (i.e., to the  $+y$  direction), with energy  $\epsilon = J > 0$ . It is given that no monomer added will extend the polymer to the left or downward.

1. A macro state of this “polymer” is characterized by  $N$  and  $m$ , where  $m$  denotes the number of monomers which extend the “polymer” upward. Find the entropy of this macro state as a function of  $N$  and  $m$ . Assume that both  $N$  and  $m$  are  $\gg 1$ , and use Stirling’s formula  $\ln N! \approx N(\ln N - 1)$  to simplify your result.
2. Write down the free energy of this macro-state of the “polymer”, as a function of  $N$ ,  $m$ , and the temperature  $T$ .
3. From minimizing this free energy, calculate the equilibrium value of  $m$  as a function of  $N$  and  $T$ .
4. Calculate the equilibrium value of the free energy as a function of  $N$  and  $T$ , and from which, calculate the specific heat of this “polymer” as a function of  $N$  and  $T$ . (Note: Simplify your expression for the free energy to something quite simple before calculating specific heat! *Make sure your result has the right dimension, or else you get no credit for this point.*)
5. Show that in the limit  $k_B T \gg J$ , the specific heat of this “polymer” is inversely proportional to  $T^2$ , and obtain the coefficient of proportionality.

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**Problem 160**


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1. Explain why a three dimensional ideal Bose gas exhibit Bose-Einstein condensation at finite temperature, and yet in two or one dimension, an ideal Bose gas cannot undergo a Bose-Einstein condensation at any finite temperature. (Or, to put it in another way, they can only undergo the transition at  $T = 0$ , which is of course, meaningless, since the absolute zero temperature can never be reached.)
2. Show that in two-dimensions, the relation between the chemical potential  $\mu$ , the total number of particles  $N$ , and the absolute temperature  $T$ , of an ideal gas, can be evaluated in close form (i.e., with the momentum or energy integral doable in close form).

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**Problem 161**

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Consider a system of fixed volume  $V$  in thermal equilibrium with a reservoir at temperature  $T$ .

1. Evaluate the mean-squared fluctuations in the system's energy

$$\langle (\Delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle$$

in terms of its partition function  $Z(T, V)$ .

2. Show that these mean-squared fluctuations may be expressed in terms of the system's heat capacity as

$$\langle (\Delta E)^2 \rangle = k_B T^2 C_V$$

3. How does the ratio of the RMS fluctuation to the mean energy depend on the number of particles if the system is a classical ideal gas?
4. By expanding  $S(E, V)$  in a Taylor series around the mean energy  $\langle E \rangle$ , find the expression for the mean-squared entropy fluctuation  $\langle (\Delta S)^2 \rangle$  in terms of the heat capacity  $C_V$  and the Boltzmann constant  $k_B$ .

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**Problem 162**

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1. Find an expression for the chemical potential  $\mu_g$  of an ideal gas as function of  $P$  and  $T$ .
2. Consider an absorbent surface having  $N$  sites, each of which can adsorb one gas molecule. This surface is in contact with an ideal gas with chemical potential  $\mu_g$  (determined by the pressure  $P$  and temperature  $T$ ). Assuming that the absorbed molecule has energy  $-\epsilon_0$  compared to one in a free state, find the grand partition function (sometimes called the grand canonical sum) that describes the absorbing surface in terms of  $T$ ,  $N$ ,  $\epsilon_0$ , and  $\mu_a$ , the chemical potential of the absorbed molecules.
3. Calculate the covering ratio  $R(P, T)$ , i.e., the ratio of the absorbed molecules to the total number  $N$  of absorbing sites on the surface.  
[Hint: What is the relation between the chemical potential of the molecules in the gas  $\mu_g$  and these absorbed  $\mu_a$ ?

$$(1+x)^N = \sum_{n=0}^N \frac{N!}{n!(N-n)!} x^n$$

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**Problem 163**

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Consider a system of  $n$  classical noninteracting identical homonuclear diatomic molecules enclosed in a box of volume  $V$ , and held at temperature  $T$ . The Hamiltonian of a single molecule is taken to be:

$$H(\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2) = \frac{1}{2m} (\vec{p}_1^2 + \vec{p}_2^2) + \frac{1}{2}\kappa |\vec{r}_1 - \vec{r}_2|^2$$

where  $\vec{p}_1$ ,  $\vec{p}_2$  and  $\vec{r}_1$ ,  $\vec{r}_2$  are the momenta and positions, respectively, for the two indistinguishable atoms comprising a molecule, and  $\kappa$  is an effective spring constant. Determine the following:

1. The classical partition function for a single molecule. Express your answer in terms of the thermal wavelength,  $\lambda_{th} = h/\sqrt{2\pi m k_B T}$ .  
[ **HINT:**  $\int_0^\infty dx \exp(-ax^2) = \sqrt{\pi/4a}$  ]
2. The mean square molecule diameter  $\langle |\vec{r}_1 - \vec{r}_2|^2 \rangle$
3. The Helmholtz free energy for  $N$  molecule system.

### Problem 164

There are approximately  $(NM)^n/(n!)^2$  ways of removing  $n$  atoms from a lattice with  $N$  sites and distribute them over  $M$  interstitial sites to obtain  $n$  Frenkel defects. The energy of an atom at an interstitial site is  $+\epsilon$  relative to the energy at the lattice site, taken as zero.

1. Obtain an expression for the (Boltzmann) entropy  $S_B(E)$  of the system in the microcanonical ensemble.
2. Calculate the temperature  $T$  as a function of  $E$ , and find the most probable excitation energy  $E$  and defect number  $n$  as a function of  $T$ .  
[**Hint:** You may need to use:  $\ln N! \approx (N \ln N) - N$  . ]

### Problem 165

Consider a system of noninteracting electrons constrained to have following density of states:

$$\begin{aligned} \rho(\epsilon) &= \text{constant} = D, & \epsilon &\geq 0; \\ \rho(\epsilon) &= 0, & \epsilon &< 0; \end{aligned}$$

where  $\epsilon$  is the one particle energy, and  $\rho(\epsilon)$  is the density of states for either spin.

1. Calculate the Fermi energy  $\epsilon_F$  at temperature  $T = 0$ , in terms of  $D$  and the number of electrons,  $N$ .
2. Find  $U_0$ , the total energy of this electron system at  $T = 0$ .
3. Calculate the chemical potential  $\mu$  at arbitrary temperature  $T$ , assuming  $N$  and  $D$  are fixed. Find an expression in terms of  $D$ ,  $N$ , and  $T$  (an exact solution, rather than an expansion). Show also that your expression reduces to the result of the first part in the limit  $T \rightarrow 0$ .
4. Find  $C_V$ , the heat capacity at constant volume, in the small- $T$  limit ( $kT \ll N/D$ ) and show that  $C_V$  is proportional to  $T$  in this regime. Assume that constant volume means  $D$  does not change.  
[**Hint:** solve first for  $U - U_0$  in this limit.]

### Problem 166

The gas of  $N$  identical particles is in a volume  $V$  at temperature  $T$ . The particles interact weakly through two-body potentials

$$U_{ij} = D \exp\left((\vec{r}_i - \vec{r}_j)^2/a^2\right),$$

where  $D$  and  $a$  are constants, and  $\vec{r}_i$ 's are particles' coordinates. Determine the leading correction in  $D$  to the (Helmholtz) Free energy  $F$  of the system at high temperatures, and the resulting change in the pressure of the gas.

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**Problem 167**

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Consider a chemical reaction  $AB \rightleftharpoons A + B$ . Treating the system as a multicomponent ideal gas, show that

$$\frac{n_{AB}}{n_A n_B} = \frac{V z_{AB}}{z_A z_B}$$

where  $n_{AB}$ ,  $n_A$ ,  $n_B$  are the concentrations (number of molecules per volume) for each molecule respectively,  $Z_{AB}$ ,  $Z_A$ ,  $Z_B$  are the partition functions per molecule and  $V$  is the volume. Note, that for equilibrium,  $\sum_i \mu_i dN_i = 0$  where the  $\mu_i$  are the chemical potentials of the various species and the  $N_i$  are their numbers.

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**Problem 168**

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1. Sketch the temperature dependence of the chemical potential (at fixed  $N$  and  $V$ ) in the whole temperature range from  $T = 0$  to  $T = \infty$ , for a three dimensional non-relativistic ideal Fermi gas (spin  $\frac{1}{2}$ ), and a three-dimensional ideal Bose gas (spin 0).
2. Derive, using statistical mechanics, a formula describing the high temperature limiting behaviour of each of these two curves (to leading order in the expansion only); the independent variables should be  $T$ ,  $N$ , and  $V$ , and no unknown constants should appear in your result.
3. Find the zero temperature ( $T = 0$ ) limiting values of these two curves as function of  $N$  and  $V$ , and state the qualitative initial  $T$ -dependence of these two curves as  $T$  is increased from zero.

[Hint:

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$
$$\ln N! \approx N(\ln N - 1) \quad \text{for } N \gg 1$$

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**Problem 169**

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Consider a molecular clock that can take on four angular positions  $\theta = n(\pi/2)$ , for  $n = 0, 1, 2, 3$ . Its energy is given by

$$E = -A \cos \theta$$

It is subject to thermal fluctuations at a temperature  $T$ .

1. Determine the value of  $\langle \cos \theta \rangle$ . Give the high-temperature and low-temperature limits. Interpret your results physically.
2. Determine the value of  $\langle \cos^2 \theta \rangle$ . Give the high-temperature and low-temperature limits. Interpret your results physically.

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**Problem 170**

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A system of  $N$  non-interacting Fermi particles with spin  $1/2$  and mass  $m$ , is confined to a volume  $V$ . It is at temperature  $T = 0$ . The particles have an energy-momentum dispersion given by  $\epsilon = p^2/2m$ .

1. Determine the chemical potential.



2. Determine the internal energy.
3. The original volume  $V$  adjoins a vacuum region with volume  $\delta V \ll V$ . Both chambers are thermally isolated from the environment. The Fermi gas now freely expands into the vacuum region. Assume that the internal energy as a function of the temperature can be parametrized at low temperatures by

$$U = \alpha(V) + \beta(V)T^2$$

where  $\alpha(V)$  and  $\beta(V)$  are functions of volume. Determine the final temperature of the gas after the expansion. Your answer should be expressed in terms of the functions  $\alpha(V)$  and  $\beta(V)$

4. Determine  $\alpha(V)$

5. Determine  $\beta(V)$

[ **Hint:** The following integral expressions may prove useful:

$$\int_0^\infty \frac{\phi(x)dx}{e^x z^{-1} + 1} = \sum_{k=0}^\infty \left( \frac{2^{2k-1} - 1}{2^{2k-2}} \right) \zeta(2k) \Phi^{(2k)}(\ln z) \approx \Phi(\ln z) + \zeta(2) \Phi^{(2)}(\ln z) + \frac{7}{4} \zeta(4) \Phi^{(4)}(\ln z),$$

where  $\Phi(\xi) = \int_0^\xi \phi(x) dx$ , and  $\Phi^{(2n)}(\xi) = \frac{\partial^{2n} \Phi(x)}{\partial x^{2n}}|_{x=\xi}$ .

$$\begin{aligned} \int_0^\infty \frac{x^{n-1} dx}{e^x z^{-1} + 1} &= \Gamma(n) \sum_{k=1}^\infty (-1)^{k+1} \frac{z^k}{k^n} \\ \int_0^\infty \frac{x dx}{e^x + 1} &= \frac{\pi^2}{12}, \quad \int_0^\infty \frac{x^{n-1} dx}{e^x z^{-1} - 1} = \Gamma(n) \sum_{k=1}^\infty \frac{z^k}{k^n} \\ \int_0^\infty \frac{x^{n-1} dx}{e^x z^{-1} - 1} &= \Gamma(n) \left[ \Gamma(1-n) [-\ln z]^{n-1} + \sum_{k=0}^\infty (-1)^k \xi(n-k) \frac{[\ln z]^k}{\Gamma(k+1)} \frac{z^k}{k^n} \right] \end{aligned}$$

]

### Problem 171

Consider a relativistic quantum Fermi gas, in three dimensions, with spin 1/2. The energy of a relativistic fermion is  $\epsilon = cp$ , where  $p$  is the momentum.

1. Find an integral expression for the internal energy  $U$  of such a gas.
2. Find the equation of state relating volume, pressure and internal energy of this gas.  
[**Hint:** Find an expression for the thermodynamic potential  $\Omega$  for the grand canonical ensemble, and relate this to  $U$ .]

### Problem 172

The Joule-Thomson process is the flow of a gas through a porous membrane separating two chambers, in which constant pressure  $p_1$  and  $p_2$  is maintained by external conditions. In such a process the enthalpy  $H = U + PV$  is conserved.

1. Given that a change of temperature and pressure is small, it is regulated by the derivative  $\left(\frac{\partial T}{\partial P}\right)_H$ . Show that this derivative is:

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P} \left[ T \left(\frac{\partial V}{\partial T}\right)_P - V \right]$$

- 
2. Calculate  $(\frac{\partial T}{\partial P})_H$  for the Van-der Waals gas with the equation of state:

$$(P + an^2)(1 - bn) = T_n$$

where  $n = N/V$  is the density, and  $a$  and  $b$  are positive constants (also  $1 - nb$  is supposed to be positive). In this part assume  $C_P$  is given, and leave your answer in terms of this parameter.

### Problem 173

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Find the final temperature  $T'$  of a Van-der Waals gas expanding to the vacuum when it changes its volume from  $V$  to  $V' > V$ , if the initial temperature was  $T$ . Assume that no heat is exchanged with the container. You may assume that  $C_V$  is a given constant.

For Van-der Waals gas the equation of state is

$$(P + an^2)(1 - bn) = T_n$$

where  $n = N/V$  is the density, and  $a$  and  $b$  are where  $n = N/V$  is the density, and  $a$  and  $b$  are positive constants (also  $1 - nb$  is supposed to be positive).

### Problem 174

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In the Debye model of the phonons (sound quanta) in a solid it is assumed that there exist two degenerate transverse branches and one longitudinal branch of sound oscillations. The oscillation frequencies  $\omega_t$ ,  $\omega_l$  are linear isotropic functions of the wave vector  $\omega_{l,t}(\vec{q}) = c_{l,t}q$  where  $c_l$  and  $c_t$  are the velocities of longitudinal and transverse sound, respectively. The frequencies of each branch are assumed to be limited by a maximal frequency  $\omega_D$  (Debye frequency). The value of  $\omega_D$  is determined by equating the total number of degrees of freedom  $3N_j$  ( $j$  is the number of particles per unit cell) to the number of phonon states

1. Find the total number of states for transverse and longitudinal phonons,  $N_t$  and  $N_l$ .
2. Find  $\omega_D$
3. Find the density of phonon states as a function of energy  $\epsilon$
4. Find the integral form for the energy and specific heat  $C_V$  very low temperatures and at high temperature.

### Problem 175

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Consider a system described by energy states with energies  $E_n$ . Using the canonical ensemble at temperature  $T$ ,

1. Derive an expression for the root-mean-square fluctuation of the internal energy,  $\Delta E|_{rms} \equiv \sqrt{\langle(\Delta E)^2\rangle}$  in terms of  $E_n$ , where  $\Delta E = E_n - \langle E \rangle$ .
2. Determine the relationship between the specific heat at constant volume and  $\Delta E|_{rms}$
3. How does the relative fluctuation in energy,  $\Delta E|_{rms}/\langle E \rangle$  depend on volume for large system?
4. Under what conditions might you expect the relative fluctuation in energy to be large?

**Problem 176**

Consider  $N$  particles of a non-interacting spin-1 Bose gas of mass  $m$ . They are confined in three dimensions to a volume  $V$ . Take  $\epsilon = p^2/2m$

1. In the high-temperature, low-density limit, determine the partition function, the free energy, and the entropy.
2. In 1926, Einstein predicted that, at sufficiently low temperatures, a non-interacting Bose gas can undergo condensation in which the occupation number  $N_0$  of the  $p = 0$  state is macroscopic: i.e.  $N_0/N$  is finite as  $N \rightarrow \infty$ . Taking the chemical potential to be zero, derive  $N_0/N$  as a function  $T$ . Determine  $T_E$ , the Einstein condensation temperature, from the condition that  $N_0(T_E) = 0$ .

Any integrals that arise should be put in dimensionless form, but need not be evaluated.

**Problem 177**

Consider  $N$  particles of a non-interacting spin-1/2 Fermi gas of mass  $m$  confined to a two dimensional plane of area  $A$ . Take  $\epsilon = \epsilon_0(p/p_0)^{3/2}$

1. Determine the  $T = 0$  energy of this Fermi gas.
2. Determine the  $T = 0$  surface pressure,  $\sigma$ , of the Fermi gas. This surface pressure is the force per unit length acting on the confining boundary of the gas.

**Problem 178**

Consider an atom trap containing two electrons, where such a large magnetic field is applied, so that only spin-up states are occupied. The spin-down states are inaccessibly high in energy, so they need not be considered in this problem. The lowest energy one-electron state of the trap has energy  $E_0$  and is doubly degenerate. The first excited one-electron state has energy  $E_1$  and is four-fold degenerate. To simplify the math set  $E_0 = 0$ .

1. Find the thermal average energy of the two electrons.
2. Obtain an approximate expression for the previous result in the high temperature limit, i.e.,  $|E_1 - E_0| \ll k_B T$ . Find the heat capacity of the electrons in this limit.
3. Find the thermal average energy and heat capacity of the two electrons also in the low temperature limit, i.e.  $|E_1 - E_0| \gg k_B T$

**Problem 179**

Consider a spin-1 Bose gas with energy-momentum relation  $\epsilon = v|p|$  in a space of dimensionality  $D = 1$  and  $D = 2$ .

1. In one of these spaces Bose-Einstein condensation will occur, and in the other case it won't. Determine which is which, and why. Note: For this part, you need not explicitly evaluate the integrals involved, but merely verify if they are well-behaved.
2. For the space in which Bose-Einstein condensation occurs, find the Bose-Einstein transition temperature  $T_{BE}$ . Express your results in terms of a dimensionless integral, which you need not evaluate.
3. Find the fraction of Bose-Einstein particles as a function of temperature  $T$ , for  $T < T_{BE}$ .

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**Problem 180**

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Consider a soap film supported by a wire frame of fixed length  $l$  along one direction and of varying length  $x$  along the other direction. Because of surface tension  $\sigma$ , there is a force  $2\sigma l$  tending to contract the film. Take  $\sigma(T, x) = \sigma_0 - \alpha T$ , where  $\sigma_0$  and  $\alpha$  are independent of  $T$  and  $x$ .

1. In one sentence, explain why the force is  $2\sigma l$ , rather than  $\sigma l$ .
2. Express the energy change  $dE$  of the film due to work  $\delta W$  associated with the surface tension and heat  $\delta Q$  absorbed by the film through the atmosphere.
3. Calculate the work  $W$  done on the film when it is stretched at a constant temperature  $T_0$  from length 0 to  $x$ .
4. Calculate the entropy change of the film when it is stretched at constant temperature  $T_0$  from length 0 to  $x$ .
5. Calculate the change in energy  $\Delta E = E(x) - E(0)$  when the film is stretched at constant temperature  $T_0$  from length 0 to  $x$ .

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**Problem 181**

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Consider a cyclic engine operating with one mole of an ideal monoatomic gas in the following reversible cycle:

$a \rightarrow b$ : expansion at constant pressure, the temperature going from  $T_a$  to  $3T_a$ .

$b \rightarrow c$ : expansion at constant temperature  $3T_a$ , the volume going to  $4V_a$ .

$c \rightarrow d$ : cooling at constant volume  $4V_a$ , the temperature going to  $T_a$

$d \rightarrow a$ : compression at constant temperature, the volume going from  $4V_a$  to  $V_a$ .

1. Sketch the cycle on a  $P - V$  diagram.
2. Find the entropy change and the change in internal energy of the gas for each part of the cycle. Find the net entropy change and the net change in internal energy over the full cycle.
3. Calculate the thermodynamic efficiency of this engine and compare it to the ideal efficiency of an engine operating between  $T_a$  and  $3T_a$ .
4. What is the net change of the entropy of the hot thermal bath during one cycle?
5. What is the net change of the entropy of the cold thermal bath during one cycle?

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**Problem 182**

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An ideal monoatomic gas is composed of  $N$  atoms each of which has additional degrees of freedom that must be taken into account when calculating the thermodynamics properties of the gas. (For example, the atoms might have electronic excited states.)

For the following questions, use  $Z_{int}(T)$  to denote the partition function of the internal degrees of freedom of a single atom and  $Z_0(T, V, N)$  to denote the canonical partition function of an ideal monoatomic gas composed of  $N$  atoms with no internal degrees of freedom.

1. Determine the difference between the Helmholtz free energy of the gas composed of atoms with internal degrees of freedom,  $F(T, V, N) = U - TS$  and the Helmholtz free energy of an ideal monoatomic gas composed of atoms with no internal degrees of freedom,  $F_0(T, V, N)$ ; i.e. determine

$$\Delta F = F(T, V, N) - F_0(T, V, N)$$

in terms of  $Z(T, V, N)$  and  $Z_{int}(T)$

2. Similarly, determine the corresponding difference in the entropies

$$\Delta S = S(T, V, N) - S_0(T, V, N)$$

3. Determine the corresponding difference in the chemical potentials

$$\Delta\mu = \mu(T, V, N) - \mu_0(T, V, N)$$

4. Determine the corresponding difference in the pressures

$$\Delta P = P(T, V, N) - P_0(T, V, N)$$

5. Evaluate  $Z_{int}(T)$  for an atom with two internal energy states separated by energy  $\Delta\varepsilon$ .

### Problem 183

$N$  spin 1/2 fermions with positive charge  $+e$  placed in a magnetic field with field strength  $B$  in the  $\hat{z}$ -direction. The single particle energy levels are Landau levels, are characterized by two quantum numbers and can be written as

$$\epsilon_n(p_z) = (n + 1/2)\hbar\omega_c + \frac{p_z^2}{2m}$$

where  $p_z$  ( $-\infty \leq p_z \leq \infty$ ) is the continuous projection of the momentum on the  $\hat{z}$  direction and non-negative integer  $n = 0, 1, 2, \dots$  is associated with the motion in  $x - y$  plane. Here  $m$  is the mass of the particle and  $\omega_c = eB/mc$  is the cyclotron frequency.

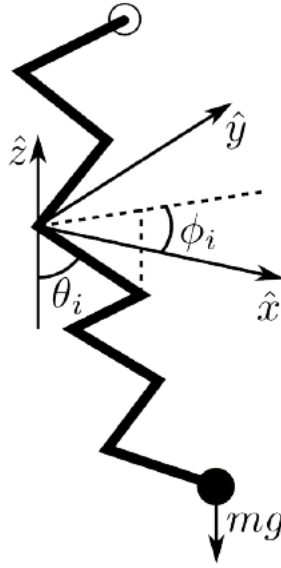
The degeneracy of each level is given by

$$g[\epsilon_n(p_z)] = \frac{m\omega_c}{2\pi\hbar} A$$

where  $A = V/L$  is the area of the system in the  $x - y$  plane,  $V$  is the volume of the system, and  $L$  is the length of the system in the  $\hat{z}$  direction.

Assuming the BOLTZMANN statistics in canonical ensemble is valid, determine

1. The equation of state.
2. The magnetization of the gas.
3. What condition on the chemical potential must be true so that the use of the Boltzmann statistics is justified?



### Problem 184

A polymer is a molecule composed of a long chain of identical molecular units, called monomers. For simplicity, assume the polymer consists of a long chain of  $N$  rod-like monomers, each of length  $l$ , attached end to end. Assume that the connectors between the monomers are completely flexible so that each monomer can make any angle with respect to its neighbors. One end of the polymer is fixed while the other end is attached to a weight ( $mg$ ) providing a constant force in the negative  $\hat{z}$  direction. Except for an arbitrary constant which can be ignored, the potential energy of any configuration of the polymer can be written as,

$$E(\theta_1, \phi_1, \theta_2, \phi_2, \dots, \theta_N, \phi_N) = \sum_{i=1}^N mgl(1 - \cos(\theta_i))$$

where  $\theta_i, \phi_i$  represent angles in the spherical coordinates that the  $i^{th}$  monomer makes with the negative  $\hat{z}$  direction. Each angle can take all possible values  $0 < \theta_i < \pi$  and  $0 < \phi_i < 2\pi$ .

1. Determine the classical canonical partition function  $Z(T, N)$  for this polymer in contact with a temperature bath at temperature  $T$ .
2. Determine the thermodynamic energy  $U(T, N)$  and entropy  $S(T, N)$  of the system. Find the temperature dependence of  $U$  and  $S$  for very small and very large temperatures.
3. If the polymer is isolated from the temperature bath and the mass at the end of the polymer is increased adiabatically from its initial value of  $m$  to a final value of  $2m$ , determine the final temperature of the polymer.

### Problem 185

A gas of  $N$  identical non-interacting, spin-1/2 fermions in three dimensions obey the dispersion relation  $\epsilon = Ap^\alpha$ , where  $p$  is the magnitude of the momentum,  $A$  and  $\alpha$  are positive constants. assuming that these particles are in a box of volume  $V$  with periodic boundary conditions.

1. Calculate the density of states of this gas as a function of  $\epsilon$ .
2. Calculate the Fermi energy of this gas as a function of  $n \equiv N/V$ , which is the density of the gas.
3. Write down as many integral expressions as needed which can, together and **implicitly**, give the internal energy  $U$  of this system as a function of  $N$ ,  $V$ , and the temperature  $T$ . You are not required to evaluate these expressions in the order to find  $U(N, V, T)$  explicitly.
4. Take the high temperature limit of the expressions you gave in the previous part, and then evaluate them in order to obtain  $U(N, T, V)$  **explicitly in this limit only**.

[Hint:  $\int_0^\infty x^{s-1} e^{-x} dx = \Gamma(s)$ ]

### Problem 186

Consider a dipole with a fixed magnitude  $\mu = |\vec{\mu}|$ , in a magnetic field  $\vec{B} = B\hat{z}$  with interaction energy  $U = -\vec{\mu} \cdot \vec{B}$ . Assume the dipole is in equilibrium with a thermal reservoir at temperature,  $T$ .

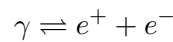
1. Without doing any calculations but using only simple physical reasoning, describe in words the behavior of  $\langle \vec{\mu} \rangle$ , the thermal average value of  $\vec{\mu}$ , in the limit as the temperature approaches zero,  $T \rightarrow 0$ .
2. If  $\vec{\mu}$  is treated classically and can point in any direction in 3-dimensional space, find  $\langle \vec{\mu} \rangle$  as a function of temperature. In particular, what are the values of  $\langle \mu_x \rangle$ ,  $\langle \mu_y \rangle$ ,  $\langle \mu_z \rangle$ ? Show that as  $T \rightarrow 0$ ,  $\vec{\mu}$  has the behavior predicted in the previous part.
3. Now assume that magnetic moment is that of a spin-1/2 particle with non-vanishing gyromagnetic ratio  $\gamma$ , so it can only point parallel or anti-parallel to  $\vec{B}$ . Find  $\langle \vec{\mu} \rangle$  as a function of temperature and show that it has the expected behavior as  $T \rightarrow 0$ . Also show that

$$\chi = \left( \frac{\partial \langle \mu_z \rangle}{\partial B} \right)_T \rightarrow \frac{\langle \vec{\mu} \rangle \cdot \vec{B}}{|\vec{B}|^2}$$

as  $T \rightarrow \infty$ . (Keep the leading non-trivial term.)

### Problem 187

Consider a box of volume  $V$  containing electron-positron pairs and photons at temperature  $T = 1/k_B\beta$ . Assume that the equilibrium is established by the process



This process does not occur in free space, but could be considered to be catalysed by the walls of the box. Ignore the walls except insofar as they allow this process to occur and answer the following questions in sequence:

1. By minimizing the appropriate potential at fixed  $T$  and  $V$  give the thermodynamic proof to show that

$$\mu_\gamma \rightleftharpoons \mu_{e^+} + \mu_{e^-}$$

which relates the chemical potentials of the three types of particles.

2. What should be the value of  $\mu_\gamma$  in view of the fact that there is no number conservation for photons?

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- What should be the values of  $\mu_{e^+}$  and  $\mu_{e^-}$  be if all the positrons and electrons in the box are due to pair creation? (Remember that a positron and an electron have the same rest mass  $m_e$ .)
  - Using the relativistic energy of the particles, write down the integral expression for the number of  $e^+$  in term of  $T$ ,  $V$ , and  $\mu_{e^+}$  and for the number of  $e^-$  in term of  $T$ ,  $V$ , and  $\mu_{e^-}$ .
  - Using the values of  $\mu_{e^+}$  and  $\mu_{e^-}$  from the third part and the integral expressions from the fourth part, calculate the mean number of electron-positron pairs, in the two limits  $k_B T \gg m_e c^2$  and  $k_B T \ll m_e c^2$ . (You may leave your answers in terms of dimensionless definite integrals.)

### Problem 188

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A box of volume  $V$  contains  $N$  molecules of a classical gas. The molecules can either be bound to the walls of the box with binding energy  $\epsilon_b$  and dispersion relation of a  $2D$  gas  $\epsilon(p) = (p_x^2 + p_y^2)/2m$ , or move freely within the volume of the box with dispersion relation of a  $3D$  gas  $\epsilon(p) = (p_x^2 + p_y^2 + p_z^2)/2m$ .

Find what portion of the molecules are stuck to the surface. Obtain an explicit results in two limiting cases of low and high temperature.

### Problem 189

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A system consists of 2 single particle states with energies  $\epsilon_0$  and  $\epsilon_1$  ( $\epsilon_0 < \epsilon_1$ ) that can be independently occupied by spin-1/2 (non-interacting) fermions.

- Determine the grand partition function for this system.
- Determine the average number of fermions in the system as a function of the temperature,  $T$ , and the chemical potential,  $\mu$ .
- Assume that the average number of particles in the system is two. Determine the limiting value of the chemical potential in the low temperature limit ( $T \rightarrow 0$ ).

[**Hint:** Convince yourself that based on the low temperature behavior of the Fermi function, the value of  $\mu$  should lie between  $\epsilon_0$  and  $\epsilon_1$ . Then determine its precise value. ]

- Assume that the average number of particles in the system is three, determine the limiting value of the chemical potential in the high temperature limit.

[**Hint:** Knowing that at the high temperatures, the particle occupancy should be described by a classical probability, determine the precise value of  $\mu$ .]

### Problem 190

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A single-particle Hamiltonian has six degenerate eigenstates at energy  $\epsilon_1$ , and another six degenerate eigenstates at energy  $\epsilon_2 > \epsilon_1$ . All other eigenstates are of very high energy relative to  $k_B T$ . Eight non-interacting identical fermions are described by this Hamiltonian. (The spin degeneracy is already included in the given degeneracies.)

- Compute the ground state energy and degeneracy for this eight-fermion system.
- Repeat for the first excited state of this system.
- Repeat for the second excited state of this system.



4. At low temperatures, where  $k_b T < 0.1(\epsilon_2 - \epsilon_1)$ , write down an approximate expression for the canonical partition function of this system, which can give the leading non-trivial-order contribution to the specific heat.
5. Repeat for the average total energy of the system.

### Problem 191

1. Derive the grand thermodynamic potential  $\Omega_G(T, V, \mu)$  for an ideal non-relativistic Maxwell-Boltzmann gas in three dimensions, assuming that the particles have no internal degrees of freedom. From the result, obtain  $S(T, V, \mu)$  and  $N(T, V, \mu)$ , and show that they obey the relation

$$S = N \left( \frac{5k_B}{2} - \frac{\mu}{T} \right)$$

2. Begin with the entropy expression for an ideal gas:

$$S = -k_B \sum_j [\langle n_j \rangle \log \langle n_j \rangle + (1 - \langle n_j \rangle) \log(1 - \langle n_j \rangle)]$$

Show that in the high temperature limit it reduces to the Maxwell-Boltzmann result obtained in the first part.

### Problem 192

A solid thin rectangular parallelepiped has dimensions  $a \times b \times b$ , where  $a \ll b$ . Assume that it has three types of acoustic vibrations (phonons), all having velocity  $v$ . Thus  $\omega = vk$  for all displacements of the form  $\vec{u} = \vec{u}_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$ , with  $\vec{u}_0$  along  $\vec{k}$  for the longitudinal mode and  $\vec{u}_0$  normal to  $\vec{k}$  for the two transverse modes.

1. Compute the total density of states  $dN/d\omega$  (number of modes per unit angular- frequency range).
2. Define the Debye frequency  $\omega_D$  by  $\int_0^{\omega_D} (dN/d\omega) d\omega = 3N$ , where  $N$  is the number of atoms. Find  $\omega_D$ . (Note, that  $N$  and  $\mathcal{N}$  have different meaning here!)
3. Assuming that  $dN/d\omega = 0$  for  $\omega > \omega_D$ , find the internal energy  $U(T)$  due to the phonons in this solid. You may express your answer in terms of a dimensionless unevaluated integral.
4. Find the specific heat  $C_V(T)$  due to the phonons in the solid. You may express your answer in terms of a dimensionless unevaluated integral.
5. Evaluate the cross-over temperature  $T_x$  below which the system must be treated as two dimensional.

### Problem 193

$N$  electrons in a box of dimensions  $L \times L \times L$  obey the energy-momentum relation  $\epsilon = p^2/2m$ , where  $m$  is the electron mass. The system is at absolute zero temperature.

1. Find the maximum occupied momentum  $p_F$  in terms of  $N$  and  $V = L^3$ .
2. Find the internal energy  $U$  of the system as function of  $N$  and  $V$ .
3. Find the pressure  $P$  from  $U$ .
4. Calculate the rate at which  $\hat{x}$  component of momentum  $p_x$  crosses a surface area  $A = L^2$  perpendicular to  $\hat{x}$  in the  $+\hat{x}$  direction due to all  $N$  electrons.
5. How does pressure relate to the rate calculated in the previous part? Give physical explanation.

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**Problem 194 Rotating Gas**

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The canonical partition function of a classical, monoatomic, ideal gas in a cylinder rotating with angular velocity  $\omega$  is given by (see Kubo chapter 2, problem 4)

$$Z = \frac{1}{N!} \left[ \pi R^2 L \left( \frac{2\pi m T}{h^2} \right)^{3/2} \frac{e^x - 1}{x} \right]^N$$

where  $x = \frac{m\omega^2 R^2}{2T}$ .

1. Find the angular momentum  $M$  of the rotating gas as a function of temperature and angular velocity.
2. Consider the limits of the obtained expression for  $M$  corresponding to very high and very low temperatures. Give the physical interpretation of obtained results. What is the criterion of high and low in this case?
3. How much energy one should supply to heat the gas from a very low temperature  $T_0$  to a very high temperature  $T_f$ ? Denote the initial angular velocity of the cylinder as  $\omega_0$ . Neglect the moment of inertia of the cylinder (vessel) itself.

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**Problem 195 Quantum Oscillator**

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A quantum particle of charge  $q$  is in the oscillator potential  $V(x) = \frac{m\omega^2}{2}x^2$  in  $1D$  at temperature  $T$ .

1. Find the heat capacity of this system.
2. Find the electric dipole susceptibility of the system. ( $d = -(\partial F / \partial E)_{V,N,T}$ ,  $\chi = (\partial d / \partial E)_{V,N,T}$ ).
3. For the oscillator state  $\psi_n$  in the presence of electric field  $E$  calculate  $x_n = \langle \psi_n | \hat{x} | \psi_n \rangle$ , and then average displacement  $\bar{x} = \sum_n x_n w_n$

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**Problem 196 Bricks**

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1. There are three identical bricks with temperatures  $T_1$ ,  $T_2$ , and  $T_3$ . You are allowed to use any number of ideal engines, but you cannot supply external heat or work to the system. What is the highest temperature you can give to one of the bricks. Give answer as a root of a single algebraic equation. (You do not need to solve the equation.)
2. Now you have  $N$  identical bricks with temperatures  $T_i$ ,  $i = 1 \dots N$ . What is the highest temperature you can give to one of the bricks. Give answer as a root of a single algebraic equation. (You do not need to solve the equation.)
3. If all of the initial temperatures are in a small interval  $T_0 < T_i < T_0 + \Delta T$ , where  $\Delta T \ll T_0$ , find the highest temperature of previous part for  $N \rightarrow \infty$ .

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**Problem 197 String**

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A  $3D$  string of length  $L$  has a temperature dependent tension  $f(T)$ .

1. What is the average value of the amplitude  $a_k^\alpha$  of the  $k$ th harmonic of a small deformation of the string?
2. What is  $\langle a_k^\alpha a_{k'}^\beta \rangle$  for two harmonics  $k$  and  $k'$ ?
3. Calculate  $\langle e^{\vec{n} \cdot \vec{a}_k} \rangle$

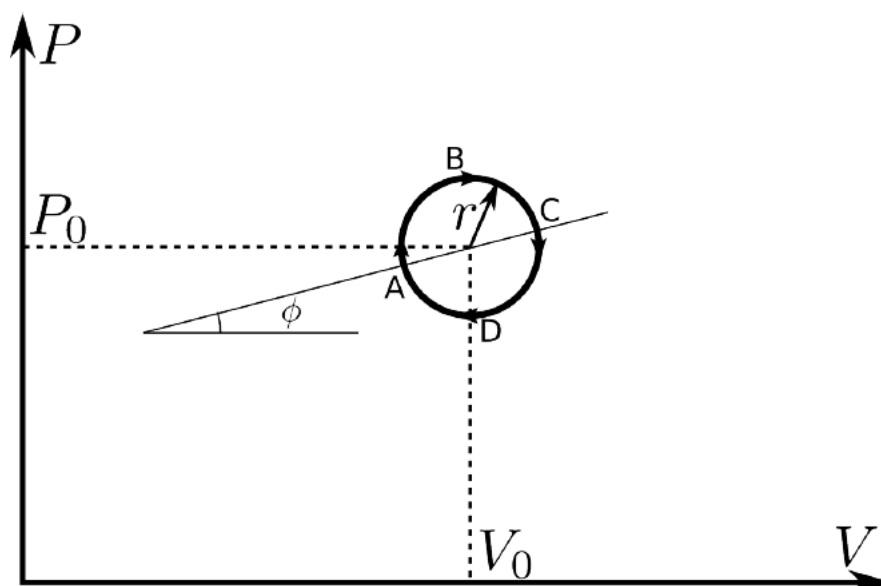
### Problem 198 Membrane

A circular membrane has a temperature dependent surface tension  $\sigma(T)$ . How does the heat capacity of the membrane depend on the small displacement  $h$  of the center of the membrane perpendicular to the membrane?

### Problem 199 Membrane

A circular membrane has a temperature dependent surface tension  $\sigma(T)$ . How does the heat capacity of the membrane depend on the small displacement  $h$  of the center of the membrane perpendicular to the membrane?

### Problem 200 Circle



A body undergoes a thermodynamic reversible cycle along the path given by

$$\frac{(P - P_0)^2}{P_0^2} + \frac{(V - V_0)^2}{V_0^2} = r^2$$

where  $r \ll 1$ . The adiabatic compressibility  $\beta_S$ , the heat capacity at constant pressure  $C_P$ , and the coefficient of thermal expansion  $\alpha$  of the body at  $P_0, V_0$  are known.

1. What is the total change of the energy of the body after a full cycle?
2. What is the total change of the entropy of the body after a full cycle?
3. What is the total work done by the body during the full cycle?
4. On the path  $ABC$  the body receives heat. On the path  $CDA$  it gives up heat. What is the angle  $\phi$  between the line  $AC$  and the axis  $V$ ?
5. What is the efficiency of this engine?
6. What would the efficiency of this engine be if the body were a monoatomic ideal gas?

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**Problem 201 Gas and vacuum**

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A cylinder of volume  $V_0 + V_1$  is divided by a partition into two parts of volume  $V_0$  and  $V_1$ , where  $V_1 \ll V_0$ . The volume  $V_0$  contains 1 mole of a gas at temperature  $T_0$  and pressure  $P_0$ . The volume  $V_1$  has vacuum. You know the gas's coefficient of thermal expansion  $\alpha(P_0, T_0)$ , its  $\beta_T(P_0, T_0)$ , and its heat capacity  $C_V(T, V)$ . At some moment the partition disappears.

1. What will be the temperature of the gas after it equilibrates?
2. A piston now adiabatically returns the gas back to the volume  $V_0$ , what will be its temperature?
3. What are these results for the ideal gas?

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**Problem 202 Distribution, average, and fluctuations**

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You throw a dice  $N$  times count the number of times you have a "3". You repeat this activity many many times.

1. With what probability the number of 3s is  $n$ ?
2. What is the average number of 3s?
3. What is the standard deviation (r.m.s. fluctuation)?

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**Problem 203 Distribution function of an oscillator**

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A classical one dimensional oscillator ( $V(x) = \frac{m\omega^2 x^2}{2}$ ) has a statistical distribution function  $\varrho(p, q) = Ae^{-E(p, q)/T}$ , where  $A$  is a normalization parameter,  $T$  is a parameter which is called temperature, and  $E(p, q)$  is the oscillator's energy.

1. Find the normalization constant  $A$ .
2. Find the average coordinate of the particle.
3. Find the average momentum of the particle.
4. Find the r.m.s. fluctuations of the particle coordinate and momentum.
5. Find the average energy of the particle. Find the heat capacity.
6. Find the distribution function for a quantity  $f = f(p, x)$ , where  $f(p, x) = p - \omega mx$

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**Problem 204 Traveling frog**

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Consider a one dimensional frog. After every  $\tau$  seconds it hops with probability  $1/2$  one meter to the left and with probability  $1/2$  one meter to the right. At  $t = 0$  the frog is at  $x = 0$ .

1. Consider a function  $p(x, t)$  – the probability for the frog to be at point  $x$  at time  $t$ . Find  $p(x, t + \tau)$ .
2. Consider a limit of large distances and long times. Find a differential equation for  $p(x, t)$ .
3. What is the initial condition for this equation?
4. Solve the equation.

5. What is the average coordinate of the frog? How does it change with time?
6. What is the average deviation of the frog's coordinate? How does it change with time?
7. Repeat all the steps for the situation when the frog hops with probability  $q$  to the left and probability  $1 - q$  to the right.

**Problem 205 Electrons in wire**

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A current  $I$  flows in the wire. Treat electrons as point like classical particles.

1. What is the probability that exactly  $n$  electrons cross through a wire cross- section in time  $T$ .
2. What is the average number of electrons which crossed a wire cross-section in time  $T$ ?
3. What is the standard deviation of that number?